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The inert gas effect on the rate of evaporation of zinc and cadmium

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THE INERT GAS EFFECT ON THE RATE OF EVAPORATION OF ZINC AND CADMIUM

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ABSTRACT

An experimental study has been made to investigate the effect of argon and helium on the rate of evaporation of zinc and cadmium under one atmosphere pressure at temperatures ranging from 500 °C to 850 °C. The experimental results were compared with the maximum rates calculated using the effusion formula as well as with values obtained using three different types of equations based on kinetic theory, diffusion theory, and empirical data. The rate of evaporation in this study appeared to be diffusion controlled.

Equations have been derived for expressing the rate of evaporation of zinc and cadmium in both argon and helium as functions of temperature of the liquid zinc and cadmium. It was found that the rates of evaporation of zinc and cadmium were higher in helium than in argon, with the difference increasing with increasing temperature. It was also found that the experimental results obtained in argon agree with the calculated values better than those obtained in helium, possibly due to slight oxidation of the cadmium.

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I. INTRODUCTION

Most previous studies of evaporation phenomena were carried out under vacuum. In this investigation the evaporation of liquid zinc and cadmium was studied under one atmosphere pressure of argon and helium at temperatures ranging from 500 °C to 850 °C. The prupose of this investigation was to study the effect of argon and helium on the evaporation of liquid metals. Previous work by Su[1] indicated that the rate of evaporation could be affected by the nature of the residual gas used. Since his work included reducing gases it was necessary to evaluate the phenomena by comparing results in only inert gases. Aside from gaining more insight into evaporation mechanisms, there is also the possibility of deriving practical benefits. If the rate is truly dependent on such things as mass or size of residual gas, and this effect differs for various metals, then it might be possible to selectively refine certain metal combinations by varying the residual gas atmosphere and pressure.

II. REVIEW OF THE LITERATURE

During the first half of the twentieth century great strides were made in the application of vapor-transport processes to extractive metallurgy. Today, vapor transport of zinc is employed not only for the retorting of zinc ores but also in refining zinc by fractional distillation, in vacuum dezincing of crude lead and in the new zinc-lead blast-furnace process.

It is possible to refine zinc electrolytically, but it is more economical in some cases to refine it by distillation. The low boiling point of zinc makes this method of refining very attractive. By using a sufficient number of redistillations a product with very high purity can be obtained.

The New Jersey Zinc Co. was the first to develop a continuous process for refining zinc by distillation. Their unit resembles a rectifier similar to that used for purifying liquids[2].

The AMAX Zinc Refiner[3], a continuously-operated, high-capacity, pyrometallurgical unit, is used by the Blackwell Zinc Co. for producing high-pruity zinc. The unit employs fractional distillation to separate zinc from its impurities, which consist principally of lead, cadmium, and iron. Essentially, the operation involves:

1. Separation of zinc from impurities having no appreciable vapor pressure at 907 °C by boiling off the zinc and volatile impurities.
2. Fractional distillation of impurities with low boiling points, and subsequent condensation of zinc.

The vaporization phenomenon can be distinguished as two processes; boiling and evaporation. Boiling is considered to be a vaporization process in which the vapor pressure of the liquid equals the pressure of

the gas phase over the liquid surface. The rate of boiling is determined by the rate of heat transfer because the latent heat of vaporization must be supplied to the boiling liquid before it can be vaporized. The vapor is removed from the liquid surface by flow or bodily movement of the gas phase as a whole rather than by diffusion. Boiling may be further subdivided into three types: nucleate boiling, transition boiling, and film boiling[4]. The outstanding feature of nucleate boiling is that bubbles form at specific, preferred points on the hot surface. In other words, active nuclei exist on the surface of the solid container. No one has determined what an active point is, but photographic evidence that something is special about certain points on the solid surface is convincing. For transition boiling, no active centers exist. The heat flux from the hot solid to the boiling liquid decreases continuously as the temperature-difference driving force is increased. During film boiling, there is a real film of vapor which coats the hot solid. Although the boiling of zinc was not investigated in this work, it is important in the commercial refining of zinc.

Evaporation is a vaporization process in which the vapor pressure of the liquid is less than the pressure of the gas phase in contact with the liquid. The rate of evaporation is not controlled by the rate of heat transfer, but by the rate of removal of vapor from the liquid-vapor interface region. This process can be devided into two steps. The first step is the transfer of matter from liquid to gas across the interface, and the second step is movement of the gas away from the interface.

The maximum rate at which molecules of a vapor can leave the surface of a liquid during evaporation is given by the effusion formula, derived from the kinetic theory of gases [5]

$$W_o = P_o(M/2\pi RT)^{1/2} \qquad (1)$$

where

W_o is the rate of evaporation in gm/cm^2-sec,

P_o is the vapor pressure of the liquid at temperature T in dynes/cm^2,

M is the molecular weight of the liquid, in gm,

R is the gas constant, in dynes/mole-degree Kelvin,

T is the absolute temperature, in degrees Kelvin.

The maximum evaporation rate would be obtained if a perfect vacuum could be maintained over the liquid. When the liquid evaporates into a perfect vacuum all the atoms leaving the liquid phase escape, that is, none of the vapor atoms return to the liquid phase.

In order to account for the probability that some of the molecules (with sufficient velocity to evaporate, moving normal to the evaporating surface) are "reflected" during evaporation, Knudsen[6] has inserted alpha, the "evaporation coefficient" into equation (1). The evaporation coefficient, alpha, is, therefore, defined as the ratio of the evaporation rate measured experimentally and the maximum evaporation rate which is obtained by independent equilibrium measurements. Most of the early evaporation rate studies were done on metals which evaporate as monatomic gases, for which alpha is close to unity. Since zinc and cadmium evaporate as monatomic gases, it was assumed that the evaporation coefficients in this investigation were unity.

The rate process of a gaseous molecule condensing on its own liquid surface involves the disappearance of one gaseous molecule and an increase in the number of bulk liquid molecules but the number of surface molecules remains unchanged. Since metals usually have a comparatively high binding energy, it is not surprising that Rapp et al.[7] found accommodation coefficients within experimental error of unity for cadmium on cadmium substrate

and zinc on zinc substrate. The accommodation coefficient can also be defined as the ratio of the number of atoms reevaporated to the total number of atoms striking the liquid surface. Knudsen gave the name "accommodation coefficient" to the ratio of the heat actually carried away by the gas, to that which would be carried if thermal equilibrium were reached.

Evaporation in the presence of a foreign gas is discussed in a number of papers[8][9][10]. Under these circumstances the phase transition is followed by diffusion into the foreign gas. In the case of steady-state conditions both processes, the phase transition and the diffusion, occur at the same rate.

The expression for the maximum rate of evaporation can be simplified by inserting the values for the constants in equation (1) to obtain

$$W_o = P_o(M/2\pi RT)^{1/2}$$

$$= P_o[M/(2\rho(3.14)(8.31)(10)^7(T)]^{1/2}$$

$$= (43.74)(10)^{-6}(P_o)(M/T)^{1/2}$$

Using the molecular weight of zinc and converting units gives

$$W_{Zn(Max)} = (43.74)(10)^{-6}(13.59)(980)(60)(P_{Zn})(65.38/T)^{1/2}$$

$$= 28.30P_{Zn}/T^{1/2} \qquad (2)$$

where

$W_{Zn(Max)}$ is the maximum rate of evaporation of zinc, in gm/cm^2-min,

P_{Zn} is the vapor pressure of zinc, in mm Hg.

Using the molecular weight of cadmium and converting units gives

$$W_{Cd(Max)} = (43.74)(10)^{-6}(13.59)(P_{Cd})(112.41/T)^{1/2}$$

$$= 36.95P_{Cd}/T^{1/2} \qquad (3)$$

where

$W_{Cd(Max)}$ is the maximum rate of evaporation of cadmium, in gm/cm^2-min,

P_{Cd} is the vapor pressure of cadmium, in mm Hg.

The measurements of the vapor pressures of zinc and cadmium by

various investigators have been compiled and evaluated by Kelley[11]. He considers that the vapor pressures of molten zinc and cadmium to be expressed best by the following equations;

$$\log P_{Zn} = \frac{-6754.5}{T} - 1.318 \log T - (0.0601)(10)^{-3}(T) + 12.723 \quad (4)$$

$$\log P_{Cd} = \frac{-5708}{T} - 1.086 \log T + 11.659 \quad (5)$$

St. Clair and Spendlove[12] pointed out that the observed rate of evaporation is always less than the maximum rate, the difference depending largely on the pressure of the residual gas in contact with the zinc. At temperatures much below the boiling point, 907 °C, the rate of evaporation of zinc is very slow at atmospheric pressure, but when the pressure of the residual gas is decreased, rapid evaporation may take place at those lower temperatures.

St. Clair and Spendlove also pointed out that the effusion formula could be used to calculate the rate of condensation of pure zinc vapor if P_{Zn} in equation (2) were replaced by the partial pressure of the zinc vapor

$$W' = 28.30\ p_{Zn}/T^{1/2} \quad (6)$$

where

W' is the weight of zinc condensed, in gm/cm^2-min,

p_{Zn} is the partial pressure of zinc vapor, in mm Hg,

T is the temperature of zinc vapor, in degrees Kelvin.

The net rate of evaporation, W_n, when pure zinc vapor is present, is the difference between the maximum rate of evaporation W_o, and the rate of condensation, W'

$$W_n = (W_o - W')$$

$$= 28.30\ (P_{Zn} - p_{Zn})/T^{1/2} \quad (7)$$

Epstein[8] has derived an equation giving the rate of evaporation of

a liquid metal in the presence of a foreign gas as

$$W_1 = \frac{2.736\ W_A T}{\lambda\ P}\ (1/b)^{2/3} \frac{(1 + M_A/M_B)^{1/2}}{[1 + (\rho_B/\rho_A)^{1/3}]^2} \qquad (8)$$

where

W_1 is the Epstein rate of evaporation of the metal A, gm/cm^2-min, into a gaseous atmosphere containing the metal A, and a residual gas B,

W_A is the maximum rate of evaporation of the metal A, gm/cm^2-min,

T is the absolute temperature, in degrees Kelvin,

P is the total pressure, dynes/cm^2,

λ is the distance between the evaporating and the condensing surfaces, cm,

M_A is the molecular weight of the metal A, gm,

M_B is the molecular weight of the residual gas B, gm,

ρ_A is the density of the metal A, gm/cm^3,

ρ_B is the densidy of the residual gas B, gm/cm^3, and

b is the Van der Waals' constant for the residual gas.

Unfortunately the Epstein equation was reported as a private communication and its derivation was not given. It was noted that the calculated rate of evaporation can be in error by a factor of 100.

Luchak and Langstroth[9][10] have derived an equation giving the rate of evaporation of a substance from a liquid surface when air is present (assuming no oxidation of the liquid surface) as

$$W_2 = (9.60)(10)^{-4}(P_o)(MD/\lambda T) \qquad (9)$$

where

W_2 is the Luchak rate of evaporation of a substance, in gm/cm^2-min,

P_o is the vapor pressure of the liquid at temperature T, in mm Hg,

M is the molecular weight of the substance being evaporated in gm,

D is the diffusivity of the substance, in cm^2/sec,

T is the absolute temperature, in degrees Kelvin,

λ is the distance between the evaporating and condensing surface, in cm.

Diffusivity, D, may be calcualted from the following equation which has been derived by Maxwell[9] from the kinetic theory of gases

$$D = \frac{kT^{2/3}(1/M_A + 1/M_B)^{1/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \qquad (10)$$

where

D is the diffusivity in the gas, cm^2/sec,

k is a constant, ranging from 0.0038 to 0.0047[13],

M_A is the molecualr weight of the metal A, in gm,

M_B is the molecular weight of the residual gas B, in gm,

P is the total pressure, in atm,

T is the absolute temperature, in degrees Kelvin,

V_A is the molal volume of the metal A in liquid state at its normal boiling point, in $cm^3/gm\text{-}mole$,

V_B is the molal volume of the residual gas B, in liquid state at its normal boiling point, in $cm^3/gm\text{-}mole$.

According to the Maxwell-Stefan[14] law of molecular diffusion, the rate of diffusion of the metal A through a residual gas B is given as follows:

$$W_3 = \frac{(60)(P)(D)(p_{A1} - p_{A2})(M_A)}{(\lambda)(R)(T_{A1})(p_{BM})} \qquad (11)$$

where

W_3 is the Maxwell rate of diffusion of the metal A, in a stagnant gas B, in gm/cm^2-min,

P is the total pressure in atm,

D is the diffusivity of the metal A in a stagnant gas B, in cm^2/sec,

p_{A1} is the partial pressure of the metal A at the evaporating surface for a given temperature T_{A1}, in atm,

p_{A2} is the partial pressure of the metal A at the condensing surface for a given te perature T_{A2}, in atm,

M_A is the molecular weight of the metal A, in gm,

λ is the distance between the evaporating and condensing surface, in cm,

R is the gas constant, 82.00(atm)(cm^3)/(mole)(deg),

T_{A1} is the absolute temperature of the metal A at the evaporating surface, in degree Kelvin,

T_{A2} is the absolute temperature of metal A at the condensing surface, in degree Kelvin,

p_{BM} is the log mean partial pressure of the residual gas B, that is, $(p_{B2} - p_{B1})/\ln(p_{B2}/p_{B1})$. where

p_{B1} and p_{B2} are the partial pressures of the residual gas B at evaporating and condensing surface respectively, in atm.

Jiro Wada and Masanobu Sasagawa[15] found that the rate of evaporation of zinc was much higher in a high-frequency induction furnace than in a resistance furnace. They also mentioned that the observed temperatures at which distillation began could be decreased by an addition of aluminum, or by the addition of a small amount of magnesium.

Su[1] used hydrogen, carbon monoxide, argon, argon-o.1 per cent

oxygen, argon-1.0 per cent oxygen and air as residual gases in a study of the factors affecting the rate of evaporation of zinc. He compared the observed rates of evaporation with theoretical values. There were a number of uncertainties in his experimental set up, such as the exact distance between the evaporating and condensing surfaces, which complicated the interpretation of his results. However, Su found that the rate of evaporation of zinc containing 0.1% aluminum was only about one-half that of the pure zinc.

III. EXPERIMENTAL

A. Apparatus:

The apparatus used in this investigation consisted of three major components: (1) resistance furnace and temperature controller, (2) evaporation unit - boiler and condenser, (3) gas purifying system.

Furnace construction

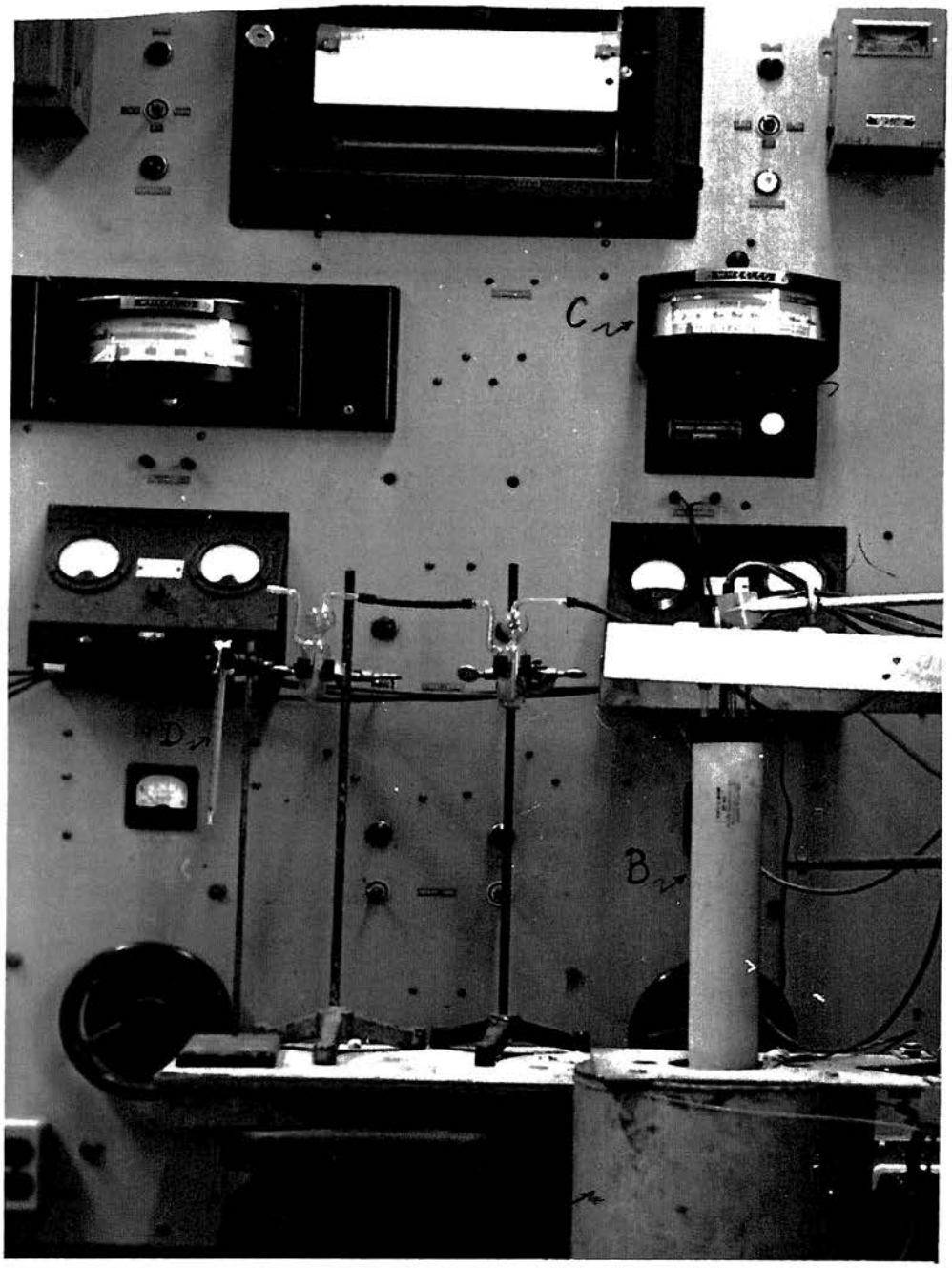
The electrically heated furnace, A, and the McDanel Zirco (Zirconium Oxide) closed end reaction tube, B , are shown in Figure 1. The Zirco tube was 28 inches long and had an internal diameter of 2.25 inches. The tube furnace was mounted vertically on a steel frame. The heating element consisted of Kanthal resistance wire wound on an alumina core. The element was covered with alundum cement. An alundum sleeve covered the entire core. The heating assembly was insulated by fire bricks and was contained in a cylindrical steel shell.

The temperature of the furnace was controlled by a Wheelco controller, C in Figure 1, using a platinum-platinum 10 per cent rhodium thermocouple. This control system held the boiler at the desired temperature $\pm$ 8 °C as indicated by a chromel-alumel thermocouple whose hot junction was between the boiler and inner surface of the Zirco tube.

The boiler

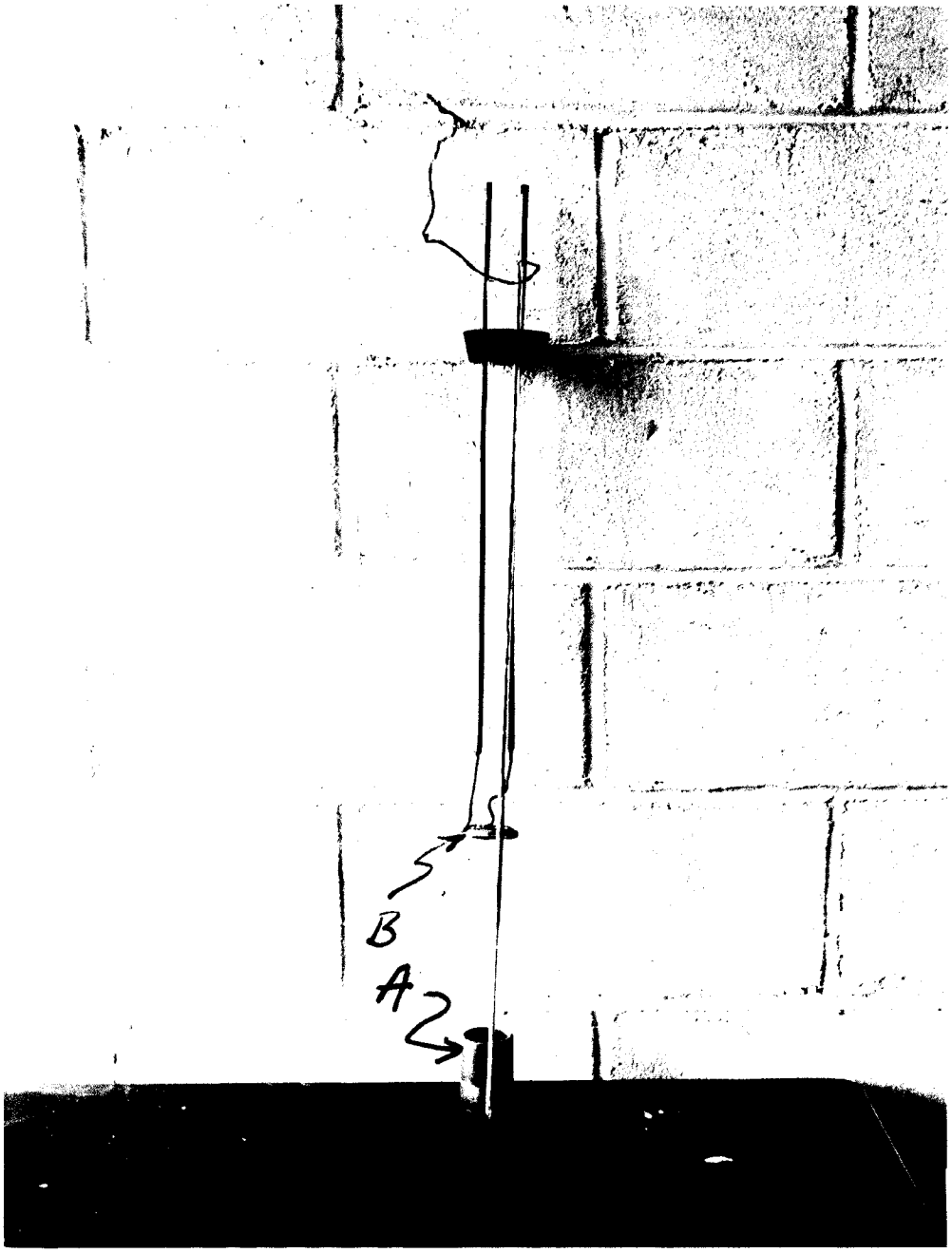
The boiler, A in Figure 2, was a graphite crucible 1.5 inches inside diameter and 2 inches deep. This gave a liquid bath with 11.4 square centimeters surface area.

A chromel-alumel thermocouple was placed beside the boiler to indicate the temperature of the molten bath during each run. This thermocouple was protected by a Vycor tube, 30 inches long and 1/4 inch outside diameter. A typical heating curve for the boiler is shown in Figure 3. The heating



A. Furnace
B. Zirco Tube
C. Wheelco Controller
D. Flow Meter

Figure 1 Furnace, Zirco Tube, and Temperature Controller



A. Boiler

B. Condenser

Figure 2 Boiler and Condenser

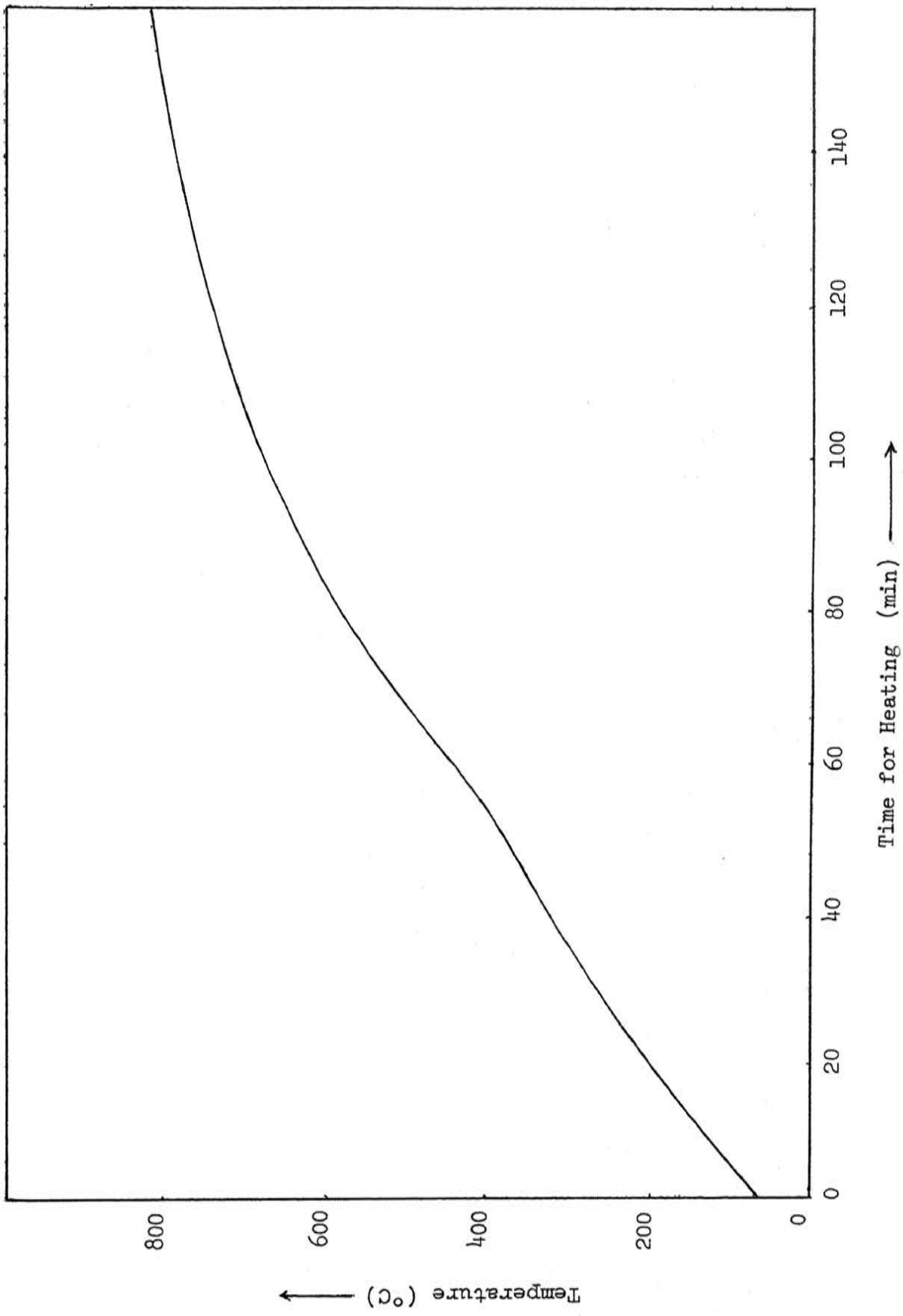


Figure 3 Typical Heating Curve of the Furnace

time to attain a given temperature was essentially constant. The variation of heating time was less than 5 minutes for runs at any given temperatures.

The condenser system

The water cooled condenser, B, is shown in Figure 2. It consisted of spiral wound, 1.8 inch diameter, copper tubing, which was silver soldered to 1.4 inch diameter copper tubing which extended through the rubber stopper for connection to the cooling water supply line and to the drain.

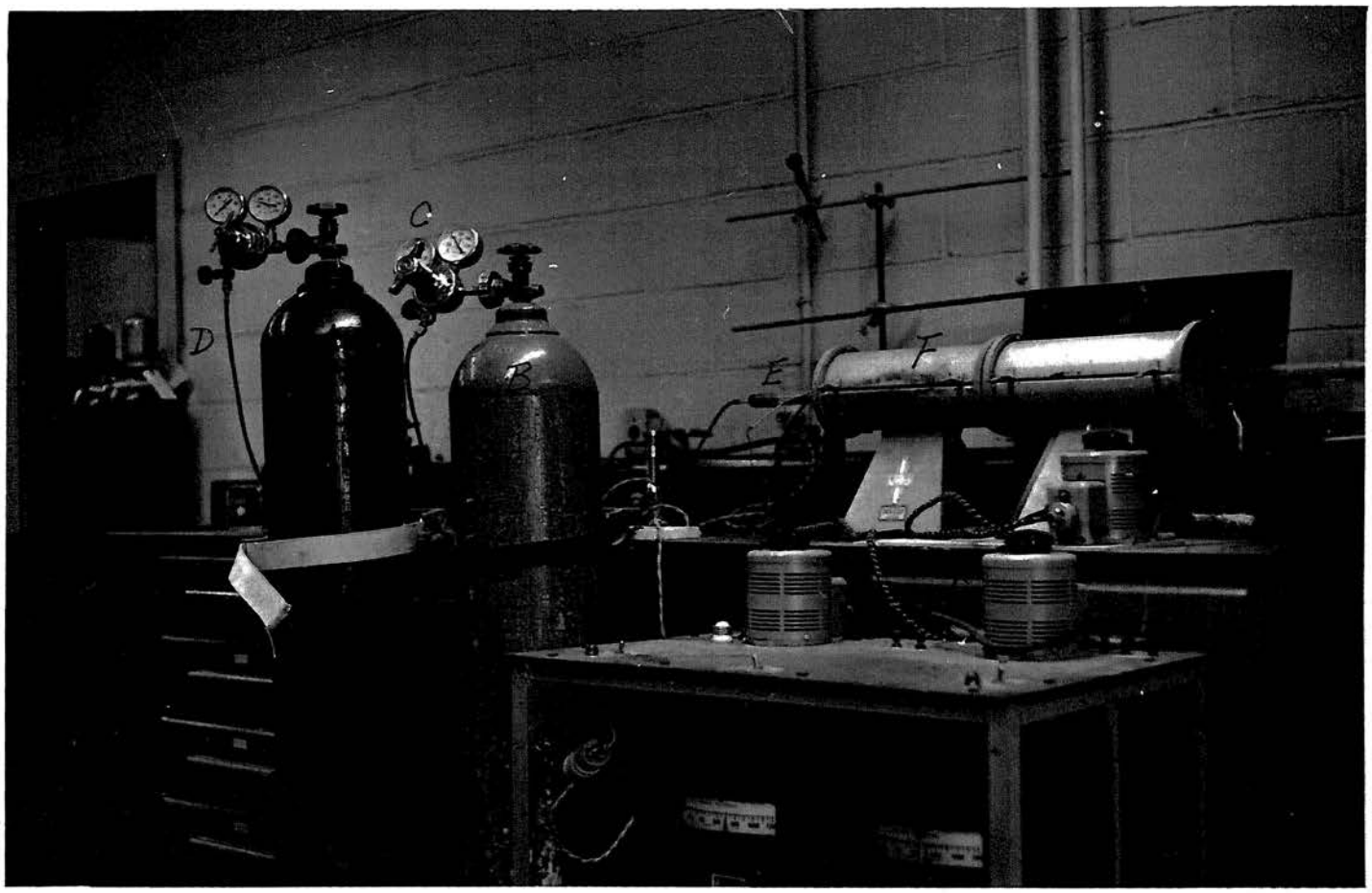
The gas atmosphere system

Argon and helium were used as the residual gases. The gas flow rate was adjusted by a needle valve on the gas cylinder to give 0.25 cc/sec. A flow meter, D in Figure 1, indicated the flow rate. Before entering the Zirco tube, the gas was purified by the system shown in Figure 4. After leaving the cylinder, the gas passed through a rubber tube into a Vycor tube one inch in outside diameter and 42 inches long E in Figure 4. The Vycor tube was filled with titanium and heated to 850 °C by two tube furnaces F in Figure 4. Oxygen and moisture in the inert gases were eliminated by this purification system. The titanium sponge was replaced and the Vycor tube was cleaned periodically or when switching from argon to helium.

The purified gas passed through a trap and then entered the Zirco tube through a tube in the rubber stopper. The gas inlet tube extended to the bottom of the Zirco tube while the gas outlet tube extended only 2 inches into the Zirco tube. After leaving the Zirco tube, the gas passed through another trap, a bubbler filled with Dibutyl Phthalate and was exhausted into the air.

B. Procedures

A schematic diagram of the apparatus is shown in Figure 5 and the



A. Argon

B. Helium

C. Needle Valve

D. Rubber Tube

E. Vycor Tube

F. Tube Furnace

G. Powerstat

Figure 4 Gas Purifying System

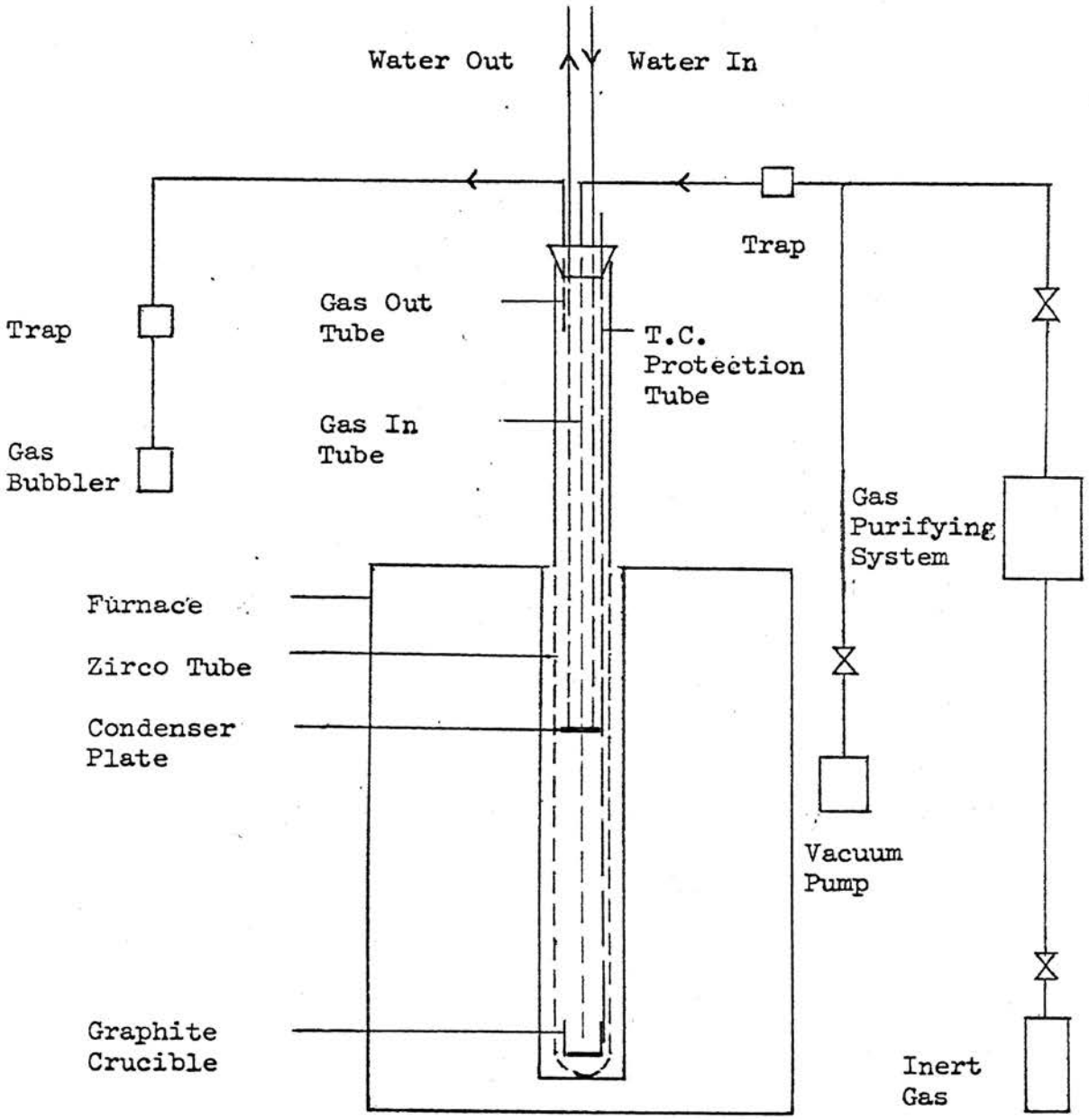


Figure 5 Schematic of the Experimental Apparatus

procedures described below were used to determine the rate of evaporation of zinc and cadmium at various temperatures below their boiling points. The evaporation of the two metals was studied in argon and helium atmospheres at a total pressure of about one atmosphere.

The analyses of starting samples of zinc or cadmium which weighed between 60 and 80 grams are given in Table I. This sample size filled the boiler to a depth of approximately 1/4 inch. The exposed liquid evaporation surface was 11.4 square centimeters.

Before placing the samples in the boiler they were filed on all surfaces to remove impurities. The samples were weighed before each run on a torsion balance with a sensitivity of $\pm$ 0.01 gram.

The distance between the condenser and liquid metal surface was fixed at 10 centimeters. Care was taken to keep the axis of the boiler vertical. If the boiler was tilted, the evaporation surface would not be perpendicular to the axis of the boiler and the surface would not be 11.4 square centimeters.

The Vycor tube with the titanium was purged with inert gas and then heated at the start of a series of runs. This tube was kept hot and gas was passed through it continuously during the experiments and during the time between experiments while the Zirco tube was being cleaned and samples prepared.

After the Zirco tube was cleaned, the boiler with weighed sample was placed inside the Zirco tube and the tube was closed by a rubber stopper and sealed by Silastic. The Zirco tube was closed off from the rest of the system and was evacuated by a vacuum pump. The purified inert gas was passed into the Zirco tube and then it was evacuated a second time. Purging with the purified inert gas was started at this time and lasted for at least 1.5 hours at room temperature. The Zirco tube was then heated to 150 °C and purging was continued at this temperature for another 0.5 hour in order to

Table I: Analyses of Metals Studied

	Zinc	Cadmium
Zn	99.99	0.010
Fe	0.0002	0.0002
Cu		0.0010
Pb	0.0019	0.005
Cd	0.0017	99.99
Th		0.0019
As		0.0001
Sn		0.001
Sb		0.001

eliminate any remaining moisture from the system. During each run, the gas flow rate was adjusted to 0.25 cc/sec and the cooling water flow rate through the condenser was 8 cc/sec.

The temperature of the boiler was measured periodically during heating by a chromel-alumel thermocouple next to the boiler wall. Zero time for an experiment was the time at which the boiler reached the desired temperature for the experiment. After the desired time at that temperature the Zirco tube was removed from the furnace and allowed to cool in still air. Inert gas and condenser water flow were maintained until the tube cooled down to room temperature.

After the Zirco tube had cooled, it was opened and the condenser and boiler were removed. The metal in the boiler and the boiler were weighed individually.

Blank runs were made for each metal at each experimental temperature and atmosphere studied in order to determine the extent of evaporation during heating and cooling. In a blank run the tube was pulled out of the furnace as soon as the proper temperature was reached. Other details of the procedure were the same as followed on a normal run.

The amount of metal vaporized was assumed to be the difference in the weight of metal added at the start of the run and the weight of the metal in the boiler after the experiment. The actual weight used in calculating the rate of evaporation was obtained by subtracting the weight loss for the appropriate blank run from the amount of metal vaporized. At lower temperatures the rate of evaporation was found to be very low, so that the evaporation time had to be longer in order to obtain a significant weight loss. At higher temperatures the time to obtain a measurable amount of evaporation was much shorter. There was a tendency for the zinc vapor to

be carried out of the Zirco tube and into the bubbler on high temperature runs. Keeping the high temperature runs short minimized this difficulty.

IV RESULTS

A series of evaporation experiments was made to determine the rates of evaporation of zinc and of cadmium in argon and helium atmospheres at various temperatures ranging from 500 °C to 850 °C. The results at each temperature are shown in Tables II to V. Blank runs were made to determine the amount evaporated during heating and cooling at each temperature and the results are also given in Table II to V. The rate of evaporation was found to be independent of the length of the run.

The evaporation rates were calculated by subtracting the appropriate blank from the amount evaporated in the experiment and dividing this difference by the product of the time and the evaporating surface area which was 11.4 square centimeters in this investigation. The weight of the crucible did not change from run to run. Therefore, it was assumed that the graphite crucible used in this investigation did not affect the rate of evaporation. The standard deviation[16] and the relative standard deviation for the evaporation rates at each temperature are given in Table VI. Sample calculations for the standard deviation and relative standard deviation are given in Appendix 1. It was found that the precision of results in this investigation was better at lower temperatures than at higher temperatures. This might be due to the fact that at higher temperatures the vapor pressure is relatively high so that the temperature factor affects the rate of evaporation much more than at lower temperatures. In other words, for the same temperature deviation the vapor pressure causes a larger error at higher temperatures than at lower temperatures.

In Figure 6 the rate of evaporation of zinc in argon and helium are plotted as Arrhenius curves, and the equations of the lines of best fit were calculated by using the least squares analysis[17]. The equation of

Table II: Evaporation of Zinc in Argon Atmosphere

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min	
A24	650	0.04	0		
A25	650	0.05	0		
A26	650	0.04	0		
A6	650	0.38	60	0.0005	
A12	650	0.36	60	0.000463	
A13	650	0.37	60	0.000478	
A14	650	0.70	120	0.000480	
A15	650	0.73	120	0.000502	
A17	650	0.69	120	0.000473	
			avg.	0.000480	$\pm 1.42 \times 10^{-5}$
			standard deviation	1.42×10^{-5}	
		relative	standard deviation	2.9%	
A1	700	0.13	0		
A7	700	0.12	0		
A29	700	0.11	0		
A39	700	0.46	30	0.000991	
A40	700	0.44	30	0.000936	
A41	700	0.46	30	0.000991	
A22	700	0.81	60	0.001007	
A28	700	0.80	60	0.000992	
A30	700	0.79	60	0.000978	
			avg.	0.000992	$\pm 3.96 \times 10^{-5}$
			standard deviation	3.96×10^{-5}	
		relative	standard deviation	3.96%	
A19	750	0.21	0		
A20	750	0.20	0		
A21	750	0.21	0		
A35	750	0.86	30	0.00193	
A36	750	0.83	30	0.00189	
A37	750	0.89	30	0.00199	
A43	750	1.45	60	0.00181	
A44	750	1.42	60	0.00178	
A45	750	1.40	60	0.00177	
			avg.	0.00186	$\pm 8.39 \times 10^{-5}$
			standard deviation	8.39×10^{-5}	
		relative	standard deviation	3.6%	

Table II: Evaporation of Zinc in Argon Atmosphere

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
A31	800	0.54	0	
A32	800	0.55	0	
A33	800	0.52	0	
A47	800	2.20	30	0.0048
A48	800	1.98	30	0.0042
A49	800	1.82	30	0.0037
			avg.	$0.00423 \pm 5.5 \times 10^{-4}$
			standard deviation	5.5×10^{-4}
			relative standard deviation	13%
A50	850	1.06	0	
A51	850	1.04	0	
A52	850	1.10	0	
A53	850	3.40	30	0.0068
A54	850	3.19	30	0.0062
A55	850	3.28	30	0.0064
			avg.	$0.00647 \pm 4.3 \times 10^{-4}$
			standard deviation	4.3×10^{-4}
			relative standard deviation	6.7%

[f] Must substract weight for zero time run (blank) to obtain evaporation rate:

Temperature °C	Average for Zero Time gm,
650	0.0433
700	0.12
750	0.2066
800	0.5366
850	1.0666

Table III: Evaporation of Zinc in Helium Atmosphere

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes		Evaporation Rate, Gm/Cm^2-Min	
C12	650	0.05	0			
C14	650	0.05	0			
C29	650	0.04	0			
C15	650	0.23	30		0.000525	
C16	650	0.22	30		0.000506	
C17	650	0.22	30		0.000506	
C19	650	0.42	60		0.000545	
C20	650	0.36	60		0.000458	
C21	650	0.39	60		0.000502	
C22	650	0.40	60		0.000516	
C39	650	0.77	120		0.000525	
C47	650	1.11	180		0.000512	
C57	650	1.73	300		0.000505	
				avg.	0.000509	$\pm 2.3 \times 10^{-5}$
			standard	deviation	2.3×10^{-5}	
		relative	standard	deviation	4.5%	
C23	700	0.12	0			
C25	700	0.10	0			
C26	700	0.13	0			
C31	700	0.14	0			
C38	700	0.12	0			
C27	700	0.514	30		0.00115	
C34	700	0.88	60		0.00111	
C61	700	1.53	120		0.00105	
				avg.	0.0011	$\pm 6.1 \times 10^{-5}$
			standard	deviation	6.1×10^{-5}	
		relative	standard	deviation	5.6%	
C24	750	0.38	0			
C32	750	0.36	0			
C36	750	0.34	0			
C43	750	1.10	30		0.00216	
C60	750	1.19	30		0.00242	
C46	750	2.02	60		0.00242	
C62	750	1.91	60		0.00226	
				avg.	0.00231	$\pm 1 \times 10^{-4}$
			standard	deviation	1×10^{-4}	
		relative	standard	deviation	4.3%	

Table III: Evaporation of Zinc in Helium Atmosphere

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
C44	800	0.84	0	
C45	800	0.81	0	
C54	800	0.80	0	
C48	800	2.65	30	0.00536
C55	800	2.46	30	0.00480
C59	800	2.77	30	0.00570
			avg.	0.00528 $\pm$ 4.25×10^{-4}
			standard deviation	4.25×10^{-4}
			relative standard deviation	8.5%
C49	850	2.09	0	
C50	850	2.08	0	
C56	850	1.93	0	
C51	850	5.12	30	0.0090
C52	850	4.97	30	0.0086
C53	850	4.95	30	0.0085
			avg.	0.00878 $\pm$ 2.8×10^{-4}
			standard deviation	2.8×10^{-4}
			relative standard deviation	3.2%

* Must substract weight for zero time run (blank) to obtain evaporation rate:

Temperature °C	Average for Zero Time gm,
650	0.0466
700	0.1220
750	0.3666
800	0.8166
850	2.0333

Table IV: Evaporation of Cadmium in Argon Atmosphere

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
F1	500	0.06	0	
F2	500	0.06	0	
F3	500	0.06	0	
F5	500	0.35	60	0.000421
F6	500	0.37	60	0.000447
F13	500	0.38	60	0.000464
			avg.	$0.000444 \pm 2.2 \times 10^{-5}$
			standard deviation	2.2×10^{-5}
			relative standard deviation	5%
F7	650	0.50	0	
F8	650	0.48	0	
F9	650	0.51	0	
F10	650	1.52	30	0.0032
F11	650	1.51	30	0.00298
F12	650	1.56	30	0.00315
			avg.	$0.00311 \pm 7.1 \times 10^{-5}$
			standard deviation	7.1×10^{-5}
			relative standard deviation	2.3%

* Must substract weight for zero time run (blank) to obtain evaporation rate:

Temperature °C	Average for Zero Time gm,
500	0.06
650	0.4966

Table V: Evaporation of Cadmium in Helium

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
G1	500	0.08	0	
G2	500	0.09	0	
G3	500	0.08	0	
G4	500	0.24	30	0.00046
G5	500	0.27	30	0.000544
G6	500	0.25	30	0.000489
			avg.	$0.000494 \pm 4.3 \times 10^{-5}$
			standard deviation	4.3×10^{-5}
			relative standard deviation	8.7%
G7	650	1.09	0	
G8	650	1.20	0	
G12	650	1.15	0	
G9	650	2.72	30	0.00461
G10	650	2.69	30	0.00452
G11	650	2.65	30	0.00443
			avg.	$0.00452 \pm 9 \times 10^{-5}$
			standard deviation	9×10^{-5}
			relative standard deviation	2%

* Must substract weight for zero time run (blank) to obtain evaporation rate:

Temperature °C	Average for Zero Time gm,
500	0.0833
650	1.1466

Table VI: Standard Deviation of the Observed Values

Metal	Boiler Temperature, °C	Residual Gas	Average Observed Rate, Gm/Cm^2-Min	Standard Deviation	Relative Standard Deviation %
Zn	650	Ar	0.00048	0.0000142	2.92
Zn	700	Ar	0.000992	0.0000396	3.96
Zn	750	Ar	0.00186	0.0000839	3.61
Zn	800	Ar	0.00423	0.00055	13.0
Zn	850	Ar	0.00647	0.00043	6.7
Zn	650	He	0.000509	0.000023	4.5
Zn	700	He	0.0011	0.000061	5.6
Zn	750	He	0.00231	0.00010	4.3
Zn	800	He	0.00528	0.000425	8.5
Zn	850	He	0.00878	0.00028	3.2
Cd	500	Ar	0.000444	0.000022	5.0
Cd	650	Ar	0.00311	0.000071	2.3
Cd	500	He	0.000494	0.000043	8.7
Cd	650	He	0.00452	0.000090	2.0

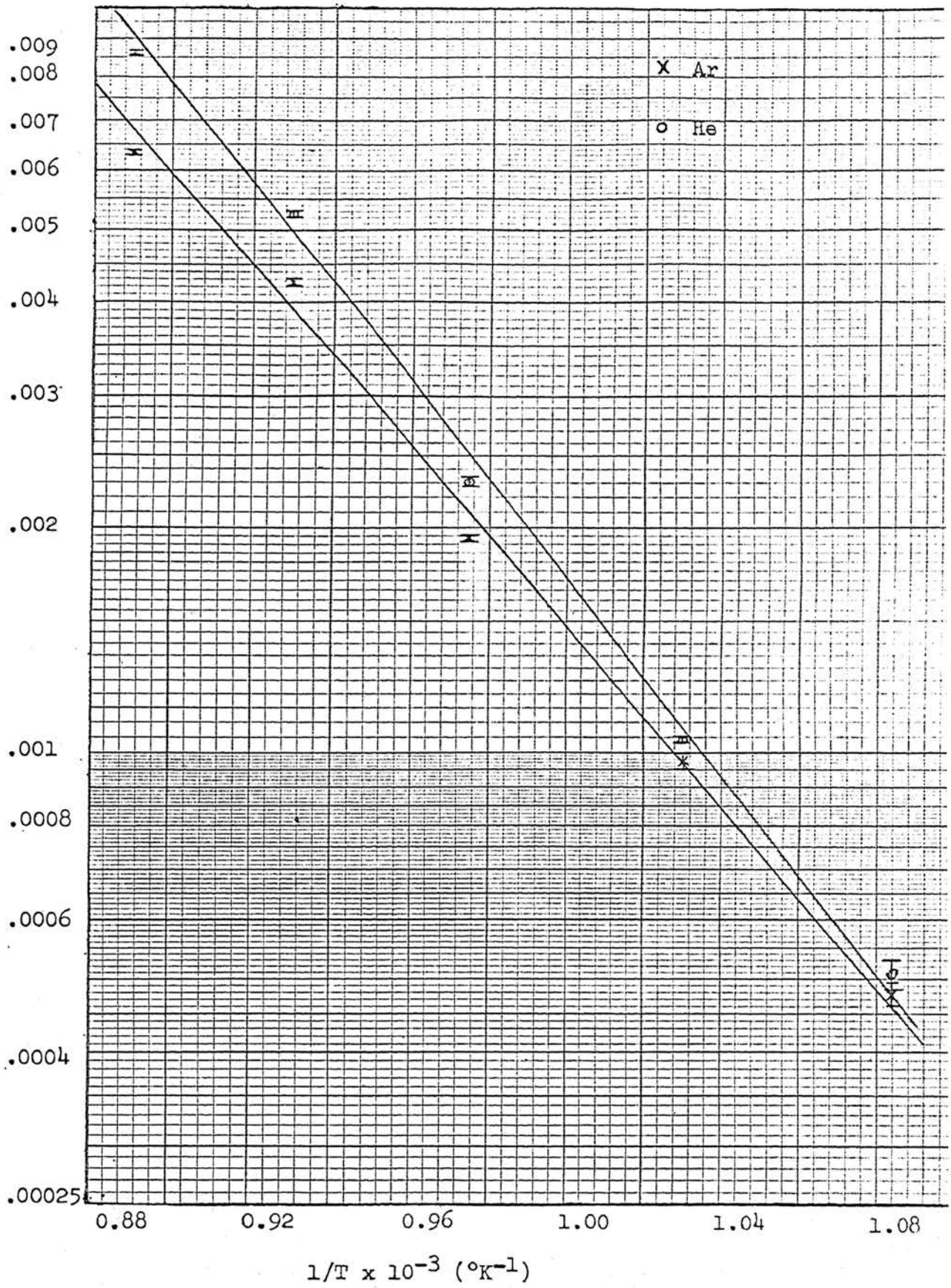


Figure 6 The Observed Rate of Evaporation of Zinc in Argon and Helium

the line that gives the relation of the rate of evaporation of zinc in helium with respect to the reciprocal of absolute temperature is given as

$$\log W_{Zn(He)} = -\frac{6555}{T} + 3.793 \qquad (12)$$

The equation for the case of argon is given as

$$\log W_{Zn(Ar)} = -\frac{6005}{T} + 3.175 \qquad (13)$$

The significance of the slope of the Arrhenius curves in this investigation is discussed in the next section. In Figure 7 the observed rate of evaporation of cadmium in both argon and helium are plotted against the reciprocal of the absolute temperature. Since there were only two temperatures studied, the least squares method was not used. It was also true in the case of cadmium that the rate of evaporation was higher in the helium than in argon. The factors that cause a higher rate in helium than in argon are again discussed in the latter part of the thesis.

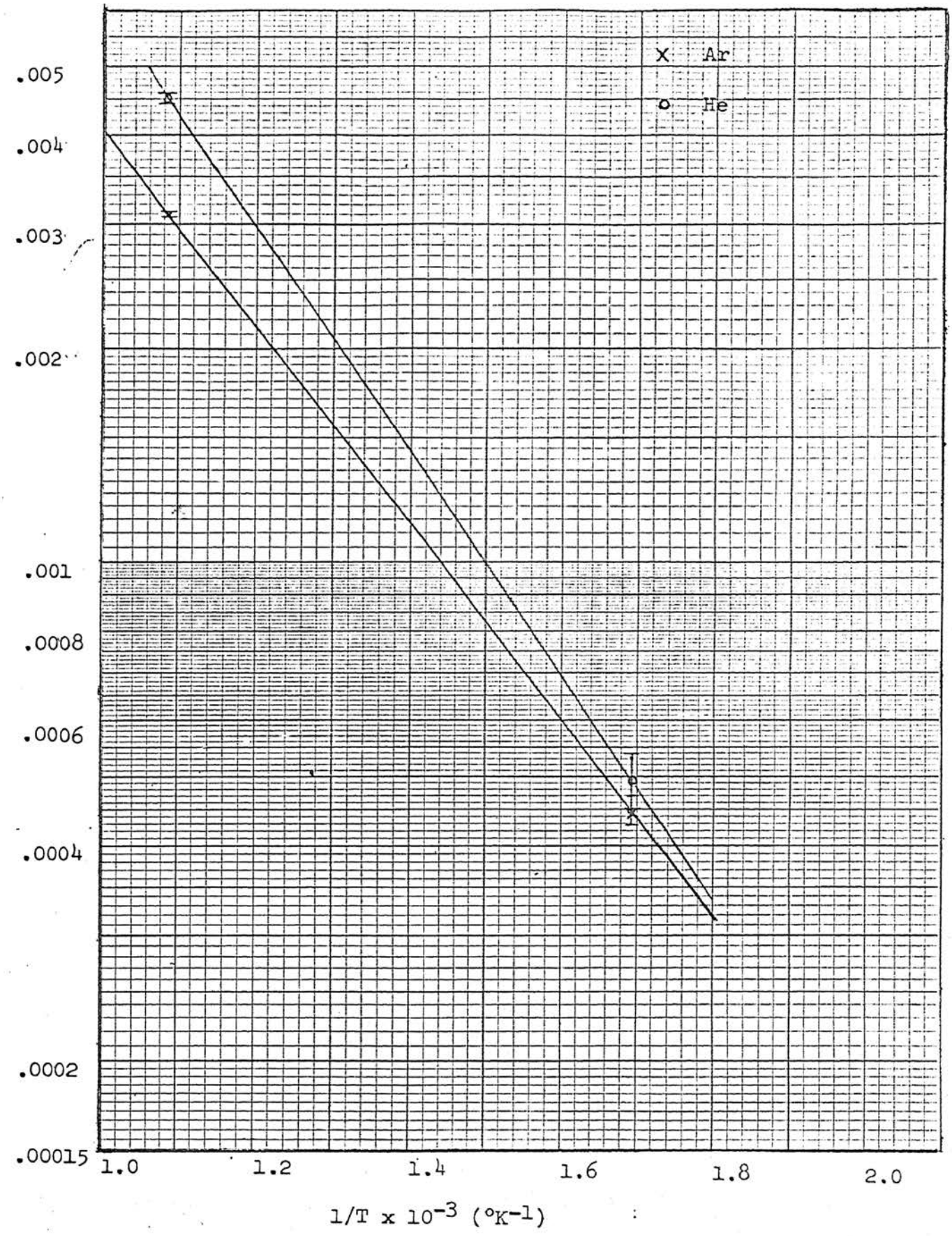


Figure 7 The Observed Rate of Evaporation of Cadmium in Argon and Helium

V. DISCUSSION

Evaporation of a metal in the presence of a residual gas is regarded as comprising three distinct parts; evaporation or escape of metal atoms from the surface, migration or movement of vapor through the residual gas, and condensation. The evaporation of zinc and cadmium at temperatures below the boiling point is probably a surface phenomenon. Hydrostatic pressure will prevent bubbles of vapor from forming at any appreciable distance below the surface.

The evaporation process can be described as one in which metal atoms diffuse through the liquid body at various velocities, depending upon the temperature. If the velocity of the atoms is great enough when it reaches the surface, it will leave the liquid phase and travel into the space above. Residual gases above the liquid metal surface form a barrier to the evaporating atoms. Collisions between the metal vapor atoms and the residual gas atoms immediately above the liquid surface causes some of the metal atoms to rebound and be returned to the liquid phase. In addition to this effect, those metal atoms that escape from the liquid phase must diffuse through the gas in order to leave the vicinity of the liquid surface. Diffusion through the gas phase is slower than moving through a space occupied only by other metal vapor atoms and free of any residual gas atoms. In the case of steady-state conditions both processes, the escape of metal atoms from the liquid phase and diffusion away from the liquid surface occur at the same rate.

In plotting the rate of evaporation versus reciprocal temperature as shown in Figure 6 and Figure 7 a straight line is obtained. From the slope of the straight line the activation energy of evaporation can be calculated. The Arrhenius equation is of the form

$$\log W = -\frac{\Delta Q}{2.303R}\frac{1}{T} + C \qquad (14)$$

where

W is the evaporation rate, in gm/cm^2-min,

T is the absolute temperature, in degrees Kelvin,

ΔQ is the activation energy of evaporation, in Kcal/mole,

R is the gas constant, cal/deg-mole,

C is an integration constant.

By comparing equations (12) and (14) we get ΔQ for zinc in helium

$$\frac{\Delta Q}{2.303R} = 6555$$

$$\Delta Q = 30.1 \text{ Kcal/mole}$$

Similarly, by comparing equation (13) and (14), the ΔQ for zinc in argon is obtained from

$$\frac{\Delta Q}{2.303R} = 6005$$

$$\Delta Q = 27.6 \text{ Kcal/mole}$$

In Figure 8 the maximum rate of evaporation of zinc calculated by equation (2) and multiplied by 10^{-5} is plotted and compared with the observed rates of evaporation of zinc in argon and helium. The line of best fit for the maximum rate is also calculated by the least squares method and is of the form

$$\log W_{Zn(Max.)} \times 10^{-5} = -\frac{5900}{T} + 2.801 \qquad (15)$$

by comparing equations (15) and (14) one gets the apparent ΔQ for zinc in vacuum for the temperature range 650 °C to 850 °C to be

$$\frac{\Delta Q}{2.303R} = 5900$$

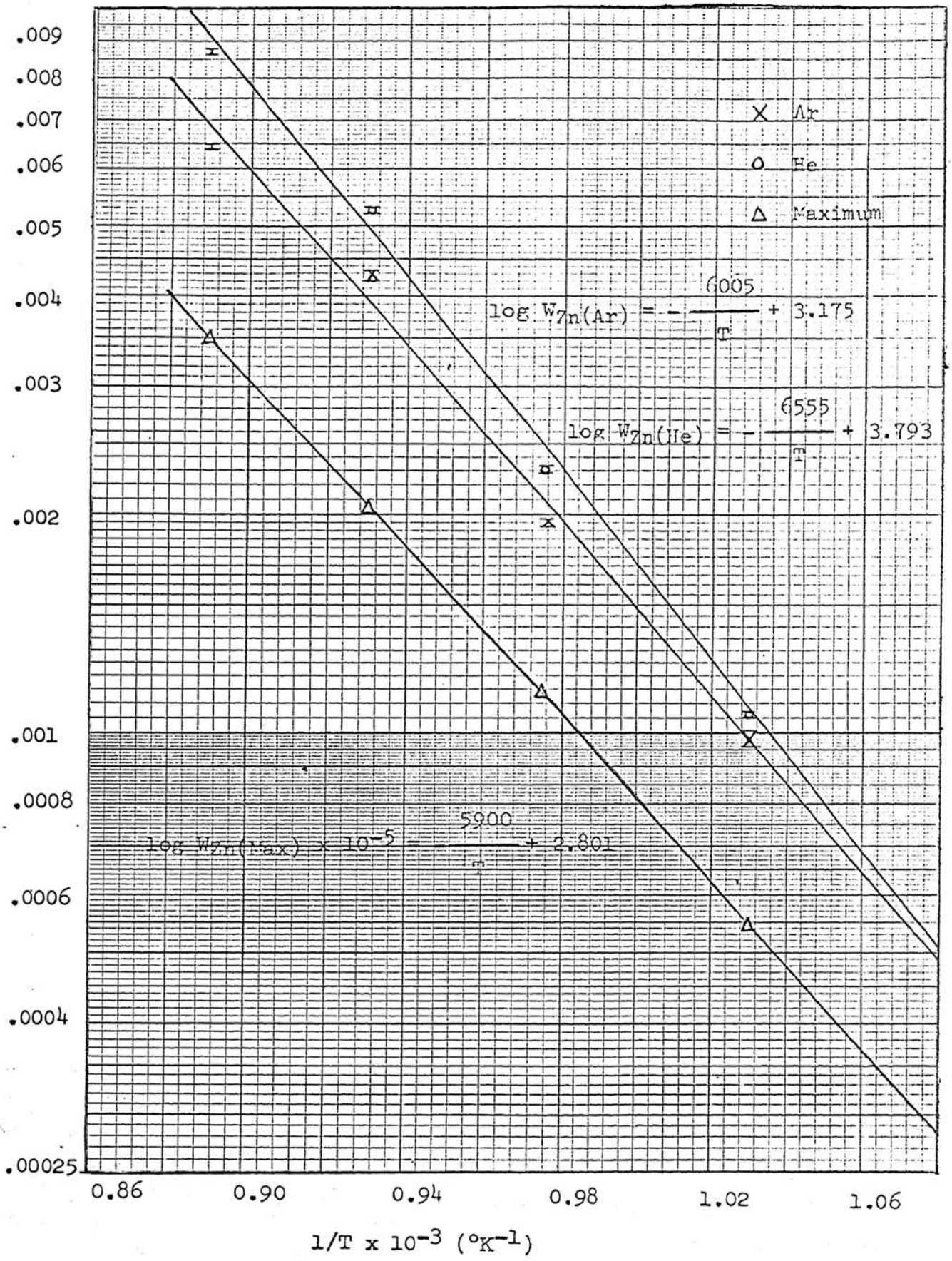


Figure 8 Comparison of the Observed Rate with the Maximum Rate of Zinc

$\Delta Q = 27.06$ Kcal/mole

The above activation energies differ from each other in the expected manner. That is, the slope of the theoretical curve is less than those of the observed curves. This is discussed below in connection with the heat of evaporation which can obtained from this data. The difference in activation energies is not believed to indicate a difference in mechanism for the evaporation processes. Lowe's[18] work shows that ΔQ is fixed for the evaporation of solid silver in oxygen, nitrogen, and vacuum. So that it seems to the author that ΔQ for zinc and cadmium should be the same in argon and helium. The fact that ΔQ_{He}, ΔQ_{Ar} and ΔQ_{Vac} are not exactly the same is probably due to the following reasons which are discussed below:

1. Contamination[19] of the evaporating surface by an oxide film.
2. The presence of adsorbed residual gas on the liquid surface might affect the local equilibrium in the activated state.[19]
3. Changes in the accommodation coefficients of the residual gases with temperature.[20]
4. Changes in the heat conductivity of the residual gas with temperatures.

A thin oxide film was always found on the surface of the sample. This oxide might come from oxygen impurity in either the inert gas or the stock from which the samples were made.

Hirth and Pound[19] noted that inert gases may be adsorbed at the liquid-vapor interface and slow the kinetics of evaporation. Since argon and helium were used in this investigation, the changes of the activation energies of evaporation of zinc and cadmium are possible.

Smoluchowski[20] found that in some gases, particularly hydrogen and helium, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving. This fraction

was called the accommodation coefficient by Knudsen.[20] He also observed that the accommodation coefficients for heavier gases, such as nitrogen, carbon dioxide were several times larger than those for lighter gases. Soddy and Berry[21] in a study of the heat conductivity of gases, found that the accommodation coefficient for argon showed an average value of 0.85 over a relatively wide temperature range; while the coefficient for helium was 0.37 at 150 °C, but became lower at higher temperatures. These variations of accommodation coefficient are recognized in the field of heat transfer as mentioned previously, and are discussed below in connection with the heat of evaporation. In this investigation, because of the lower accommodation coefficient of helium especially at higher temperatures, less heat is transferred from the liquid to the helium than to argon and the surface temperatur of the liquid metal should be higher in a helium atmosphere than in argon. Therefore, it is reasonable to believe that the metal was actually evaporatir at a higher temperature in the helium atmosphere than in the argon atmosphere even though the chromel-alumel thermocouple outside that boiler indicated the same temperature. This could account for the steeper slope on the helium curve.

If the temperature of the inert gases were higher than that of the liquid metal, heat should be transfered from the inert gases to the liquid metal. Since the heat conductivity of helium is much higher than that of argon, more heat would be transferred to the liquid phase and the temperature of the liquid surface would be higher in the helium atmosphere than that in argon. This in turn could account for the steeper slope on the helium curve.

The three equations derived by Epstein, Luchak, and Maxerll have been quoted as equations (8), (9), and (11), in the Literature Review. Typical calculations using these equations to obtain the rate of evaporation of zinc at 850 °C in argon are shown in Appendix 2.

The observed rates of evaporation of zinc and cadmium in both argon and helium and the values calculated by using the three equations and the maximum rate are given in Table VII and shown in Figure 9. The ratios of the calculated values to the observed values are given in Table VIII. It was found that the ratios of the Epstein values to the observed values increased with increasing temperature whereas the Luchak and Maxwell values remained a relatively constant fraction of the observed values at all temperatures. This tends to indicate that the Epstein equation does not agree with the data obtained in this investigation. Since the Epstein equation was reported as a private communication, its derivation is not known and further comments on the assumed mechanism of evaporation cannot be made. Since the ratios of the Luchak and the Maxwell values to the observed values show less variation with temperature, the mechanism of the evaporation of zinc and cadmium in an inert gas is probably that assumed in the derivation of the Luchak and Maxwell equations.

The observed rate of evaporation was found to be higher in helium than in argon at each temperature. This was probably caused by the following reasons:

1. Since the rate of evaporation is diffusion-controlled in this investigation, the larger the diffusivity, the higher the rate of evaporation will be. In Table IX the calculated diffusivity of zinc and cadmium vapors through argon and helium are listed. Because the value in helium is approximately 1.3 times larger than that in argon the rate of evaporation is then expected to be higher in helium than in argon.
2. As metal atoms diffuse through the residual gas, they lose energy by collision with the residual gas molecules. In Appendix 3 the forces exerted on the zinc atoms by both argon and helium molecules were

Table VII: Observed Rates and Calculated Values

Metal	Temperature °C	Residual Gas	Epstein Rate Gm/Cm^2-Min	Luchak Rate Gm/Cm^2-Min	Maxwell Rate Gm/Cm^2-Min	Observed Rate Gm/Cm^2-Min	Maximum Rate Gm/Cm^2-Min
Zn	650	Ar	8.14×10^{-5}	1.76×10^{-4}	1.90×10^{-4}	4.80×10^{-4}	25.74
Zn	700	Ar	2.74×10^{-5}	3.98×10^{-4}	4.28×10^{-4}	9.92×10^{-4}	55.21
Zn	750	Ar	7.90×10^{-4}	8.58×10^{-4}	9.86×10^{-4}	1.86×10^{-3}	109.3
Zn	800	Ar	2.04×10^{-3}	1.63×10^{-3}	1.94×10^{-3}	4.23×10^{-3}	202.2
Zn	850	Ar	5.28×10^{-3}	2.93×10^{-3}	3.54×10^{-3}	6.47×10^{-3}	352.4
Zn	650	He	6.83×10^{-4}	2.43×10^{-4}	2.63×10^{-4}	5.09×10^{-4}	25.74
Zn	700	He	2.04×10^{-3}	5.25×10^{-4}	5.92×10^{-4}	1.10×10^{-3}	55.21
Zn	750	He	5.63×10^{-3}	1.17×10^{-3}	1.35×10^{-3}	2.31×10^{-3}	109.3
Zn	800	He	1.33×10^{-2}	2.22×10^{-3}	2.68×10^{-3}	5.28×10^{-3}	202.2
Zn	850	He	2.87×10^{-2}	4.05×10^{-3}	4.97×10^{-3}	8.78×10^{-3}	352.4
Cd	500	Ar	5.41×10^{-5}	1.22×10^{-4}	1.34×10^{-4}	4.44×10^{-4}	18.37
Cd	650	Ar	2.55×10^{-3}	1.75×10^{-3}	1.99×10^{-3}	3.11×10^{-3}	219.94
Cd	500	He	9.25×10^{-5}	1.71×10^{-4}	1.87×10^{-4}	4.94×10^{-4}	18.37
Cd	650	He	5.34×10^{-3}	2.45×10^{-3}	2.80×10^{-3}	4.52×10^{-3}	219.94

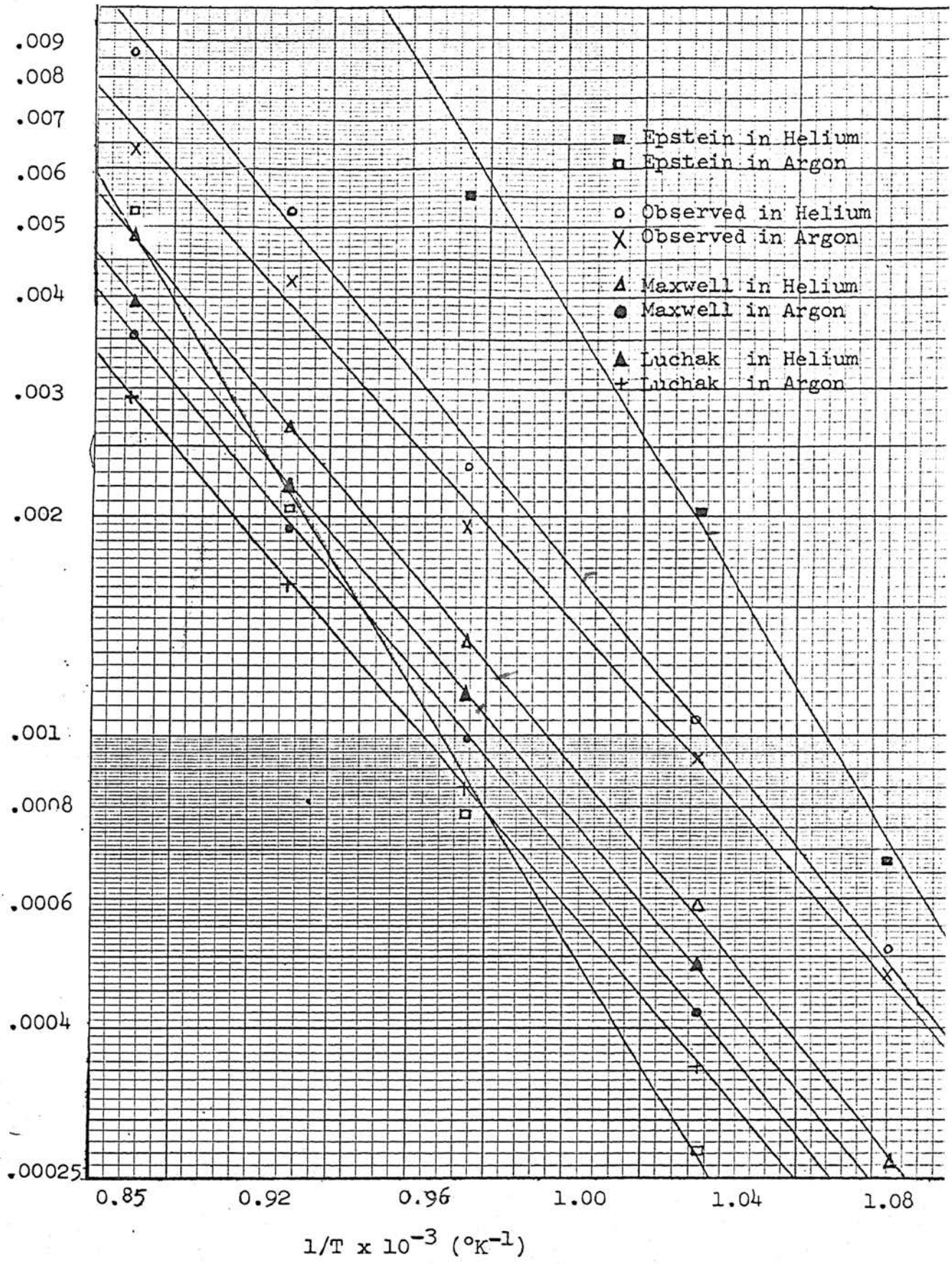


Figure 9 Comparison of the Observed and Calculated Rate of Zinc Evaporation

Table VIII. Ratio of the Calculated Values to the Observed Values

al	Temperature °C	Residual Gas	Epstein Value Observed Value	Luchak Value Observed Value	Maxwell Valu Observed Valu
n	650	Ar	0.17	0.37	0.40
n	700	Ar	0.27	0.40	0.43
n	750	Ar	0.42	0.45	0.53
n	800	Ar	0.48	0.39	0.46
n	850	Ar	0.82	0.45	0.54
n	650	He	1.34	0.48	0.52
n	700	He	1.82	0.54	0.53
n	750	He	2.44	0.51	0.58
n	800	He	2.51	0.42	0.51
n	850	He	3.29	0.46	0.56
d	500	Ar	0.12	0.27	0.30
d	650	Ar	0.82	0.56	0.64
d	500	He	0.19	0.66	0.72
d	650	He	1.25	1.02	1.15

Tavle IX. Calculated Values of Diffusivity of Metal Vapors Through Inert Gas

etal	Inert Gas	Temperature °C	Diffusivity Cm^2/Sec
Zn	Ar	650	0.937
Zn	Ar	700	1.014
Zn	Ar	750	1.093
Zn	Ar	800	1.173
Zn	Ar	850	1.257
Zn	He	650	1.296
Zn	He	700	1.402
Zn	He	750	1.511
Zn	He	800	1.623
Zn	He	850	1.738
Cd	Ar	500	0.637
Cd	Ar	650	0.831
Cd	He	500	0.891
Cd	He	650	1.163

calculated for a head-on collision. The force exerted by argon was 1.2 times larger than that by helium molecules. Thus zinc atoms lose more energy in argon than in helium. Wada concluded the same thing[22] in his study of the preparation of fine metal powders by condensing metal vapors in various gases.

3. The thermal accommodation coefficient of helium is much lower than that of argon at all temperatures. Therefore, it is possible that the temperature of the evaporating metal surface was always higher in the helium runs than in argon runs as explained above.

In Figure 10 the rate of evaporation of cadmium in argon and helium is compared to the maximum rate. The method of least squares was used to obtain the equation of the maximum rate curve. This was

$$\log W_{Cd(Max)} \times 10^{-5} = -\frac{5158.3}{T} + 2.937 \qquad (16)$$

The 650 °C rate in argon could be low. The slope of the argon curve might indicate this. Furthermore, a thicker oxide film was observed on the cadmium after the 650 °C runs in argon than was observed after the runs at 500 °C. Since the evaporation of cadmium was studied at only two temperatures it is difficult to discuss the evaporation process quantitatively as has been done for zinc.

In figure 11 both the calculated maximum rate and the observed rate of evaporation in argon are plotted for the two metals against the reciprocal temperature. In the absence of oxidation the slope of the observed curve for the evaporation of cadmium in argon would be steeper and this implies that argon decreases the evaporation rates of both cadmium and zinc by the same factor at all temperatures. Figure 12 indicated that helium has nearly the same effect on the rates of evaporation of zinc and cadmium.

Thermodynamic considerations can also give us a relationship between

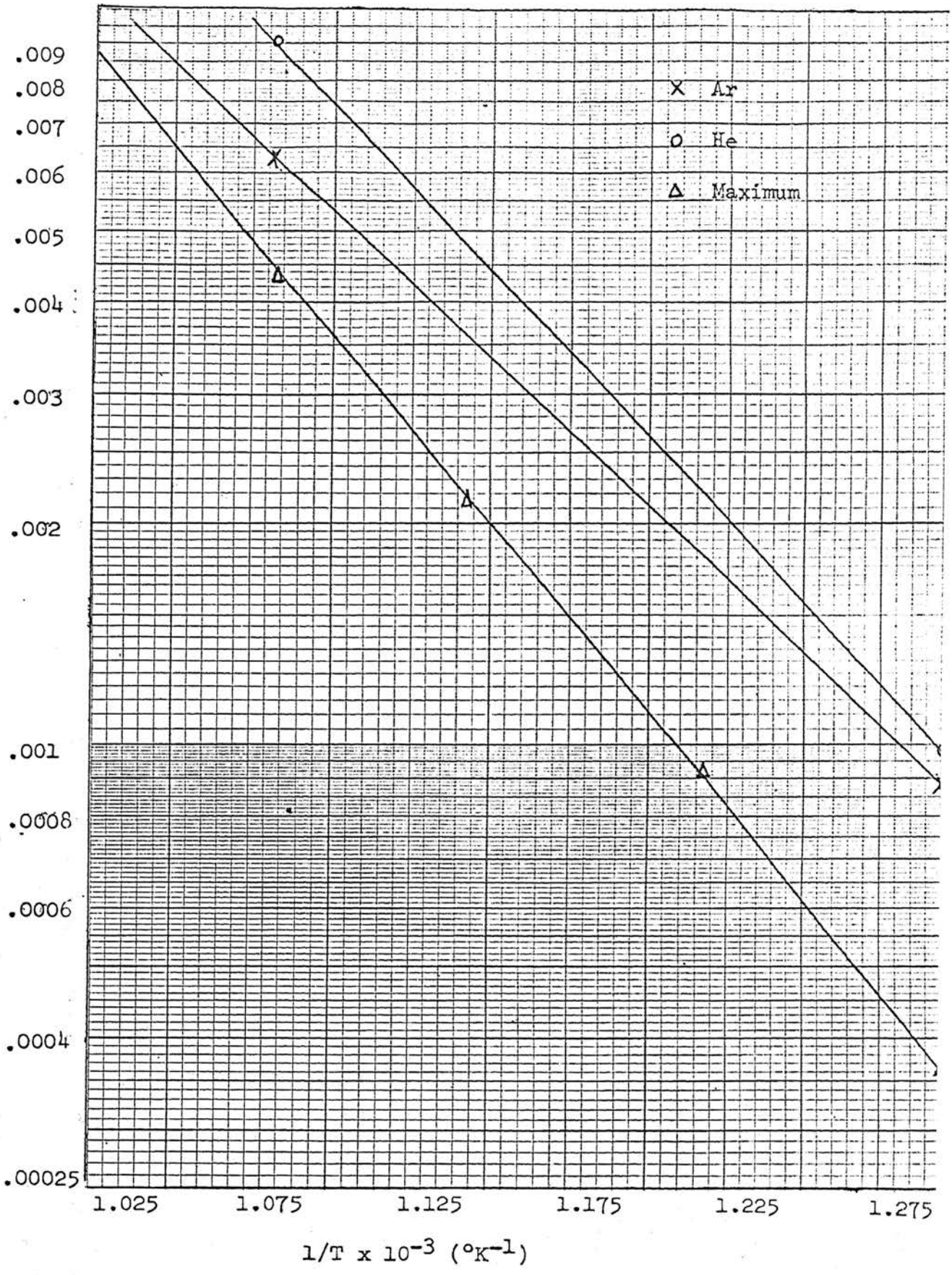


Figure 10 The Observed and the Maximum Rate of Evaporation of Cadmium

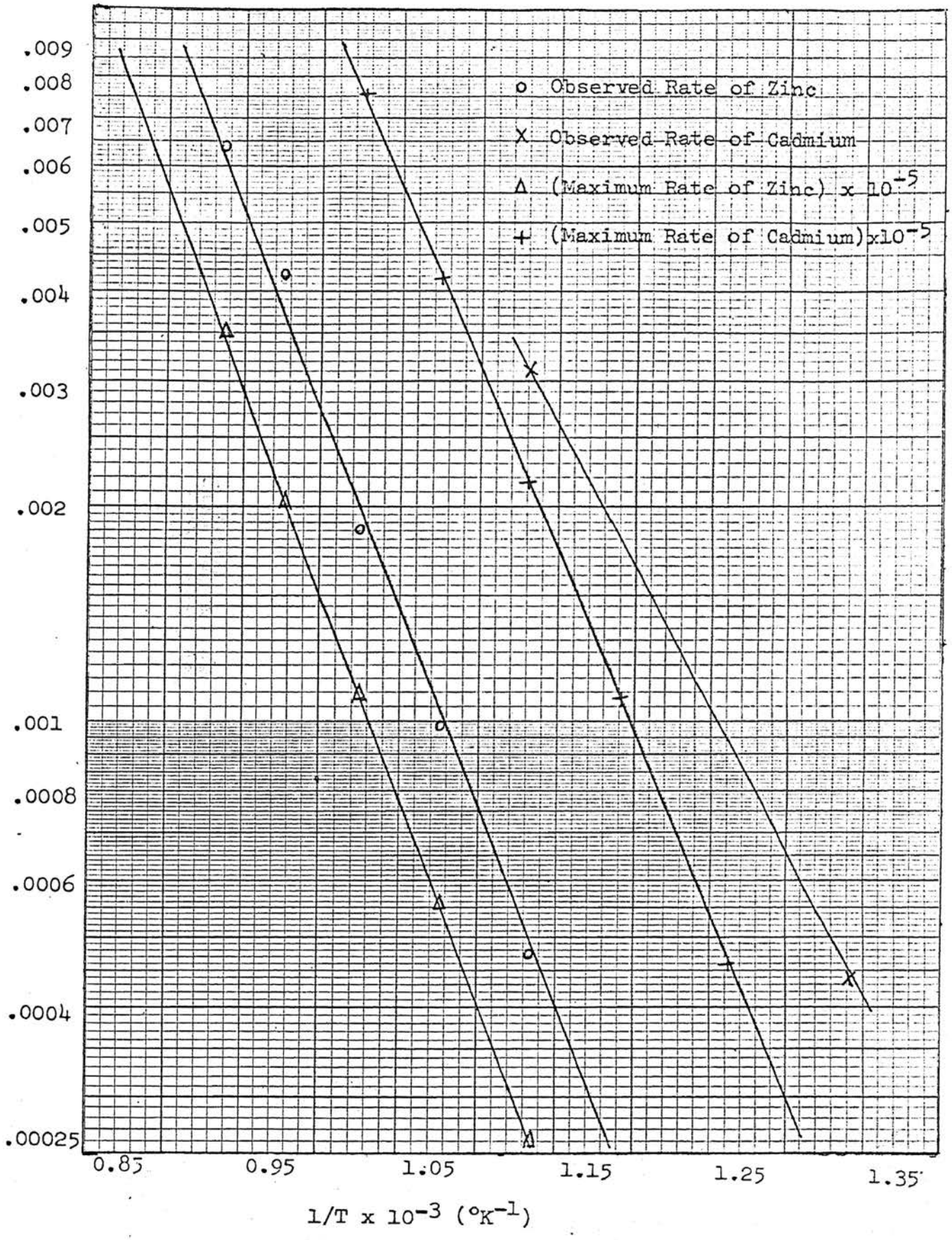


Figure 11 Comparison of The Rate of Evaporation of Zinc and Cadmium in Argon

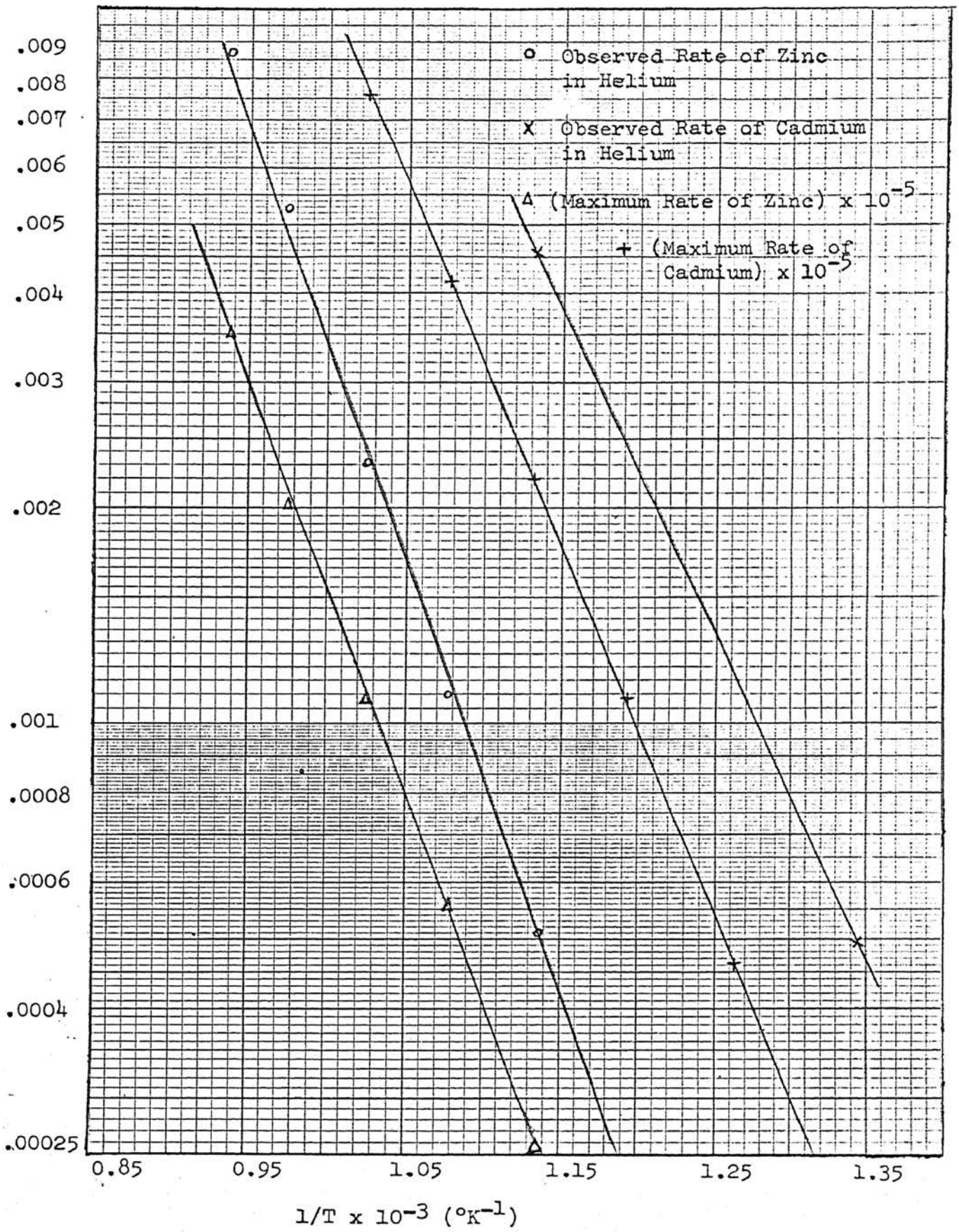


Figure 12 Comparison of the Rate of Evaporation of Zinc and Cadmium in Helium

te of evaporation and temperature. The Clausius-Clapeyron equation is

$$\Delta H = T \frac{dP_o}{dT}(V_G - V_L) \qquad (17)$$

ere

ΔH is the latent heat of evaporation per mole of zinc,

V_G is the volume of zinc vapor, and

V_L is the volume of liquid zinc.

ice V_L is negligibly small compared to V_G and if the gas phase is assumed be ideal $V_L = 0$ and $PV = RT$. The Clausius-Clapeyron equation becomes

$$\frac{d\ln P_o}{dT} = \frac{\Delta H}{RT^2} \qquad (18)$$

general, ΔH is a function of temperature such that

$$\frac{d(\Delta H)}{dT} = C_{P(V)} - C_{P(L)} \qquad (19)$$

ere $C_{P(V)}$ and $C_{P(L)}$ are the heat capacities of zinc vapor and liquid ic respectively. Since zinc evaporates as monatomic vapor its heat pacity at constant pressure is

$$C_{P(V)} = 2.98 + R = 4.98 \quad \text{cal/gm-atom}$$

e heat capacity of liquid zinc $C_{P(L)}$ is 7.5 cal/gm-atom according to lley[11]. Substituting $C_{P(L)}$ in equation (19) and integrating obtain

$$\Delta H = \Delta H_o - 2.54T \qquad (20)$$

ere ΔH_o is an integration constant.

bstituting (20) in (18) and integrating again, we obtain

$$\log P_o = A - \frac{0.218\,\Delta H_o}{T} - 1.28 \log T \qquad (21)$$

ere A is a constant of integration.

cing the logarithm of equation (1) for zinc gives

$$\log W_{Zn} = \log P_o + 1/2(\log M_{Zn}/2\pi R) - 1/2 \log T \qquad (22)$$

)ining this with (21),

$$\log W_{Zn} = A' - \frac{0.218\Delta H_o}{T} - 1.78 \log T \qquad (23)$$

:e $A' = A + 1/2 \log \frac{M_{Zn}}{2\pi R}$ (24)

Equation (23) gives us the rate of evaporation of zinc as a function :he temperature. There are two empirical constants A' and ΔH_o to be :rmined from the experiments. Equation (23) shows that for zinc)g W_{Zn} + 1.78 log T) is a linear function of 1/T. In Figure 13 the ıtity (log W_{Zn} + 1.78 log T) for the evaporation of zinc in argon, heliur perfect vacuum are plotted against 1/T. The lines of best fit were :ulated by the least squares method. The slopes of these lines are :l to the quantity $0.218\Delta H_o$. The equation of the line for the evaporatior :inc in argon was found to be

$$\log W_{Zn(Ar)} = -\frac{7070.6}{T} - 1.78 \log T + 9.5758 \qquad (25)$$

e $0.218(\Delta H_o)_{Ar} = 7070.6$,

. $(\Delta H_o)_{Ar} = 32.4$ Kcal/mole

larly, the equation for zinc in helium was found to be

$$\log W_{Zn(He)} = -\frac{7301.7}{T} - 1.78 \log T + 9.8836 \qquad (26)$$

since $0.218(\Delta H_o)_{He} = 7301.7$,

$(\Delta H_o)_{He} = 33.5$ Kcal/more.

perfect vacuum the equation for the rate of evaporation of zinc was d to be

$$\log W_{Zn(Max)} = -\frac{6709}{T} - 1.78 \log T + 8.95 \qquad (27)$$

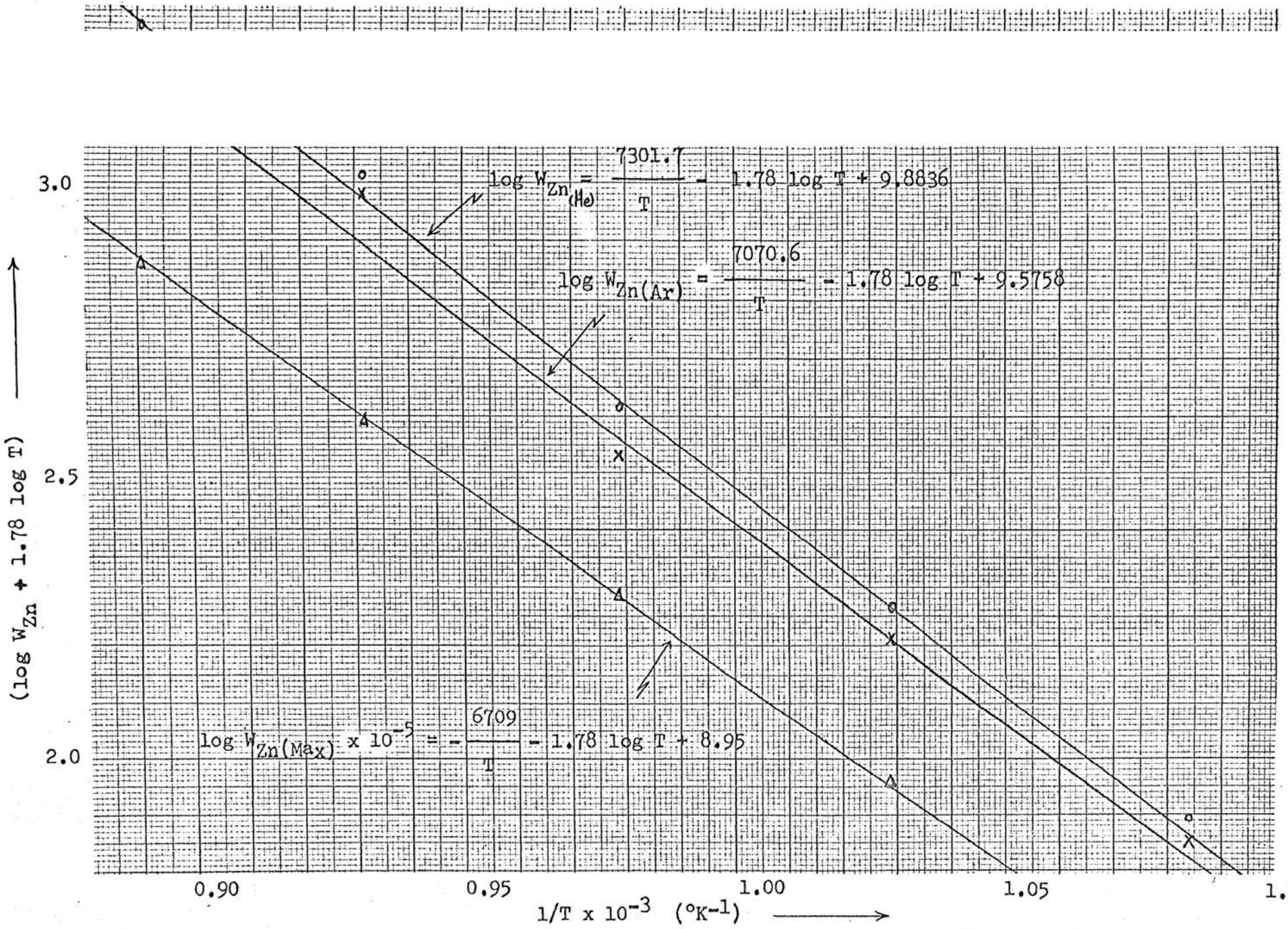


Figure 13 (log W_{Zn} + 1.78 log T) in Argon, Helium, and Vacuum vs 1/T

e $0.218(\Delta H_o)_{vac} = 6709$,

$(\Delta H_o)_{vac} = 30.7$ Kcal/mole

At the boiling point of zinc, 907 °C, ΔH is the heat of vaporization

From Equation (20) we have

$\Delta H_v = \Delta H_o - 2.54 \times 1180$

rgon $(\Delta H_v)_{Ar} = 32.4 \times 10^3 - 2.54 \times 1180$

$= 29.4$ Kcal/mole

elium $(\Delta H_v)_{He} = 32.5 \times 10^3 - 2.54 \times 1180$

$= 30.5$ Kcal/mole

perfect vacuum $(\Delta H_v)_{vac} = 30.7 - 2.54 \times 1180$

$= 27.7$ Kcal/mole

The heat of evaporation of zinc obtained from the data from the argon is closer to the theoretical value (vacuum value) than is the value d on the helium runs. It has been found[23] that this is generally case. Latent heats determined in atmospheres of heavier gases agree the theoretical value better than the same latent heat determined in tmosphere of lighter gases. The better agreement when using heavier s is attributted to the decrease in the accommodation coefficient of ter gases at higher temperatures.[20][24][25]

The variation of the observed rates of evaporation of cadmium with erature can be derived by the same thermodynamic approach used for . In Figure 14 ($\log W_{Cd} + 1.58 \log T$) is plotted against the reciprocal erature for cadmium. The line drawn through the points representing naximum rates of evaporation of cadmium is found by the least squares od to be

$$\log W_{Cd(Max)} = -\frac{5754.8}{T} - 1.58 \log T + 8.267 \qquad (28)$$

Because of the inadequate data for cadmium, the least squares method

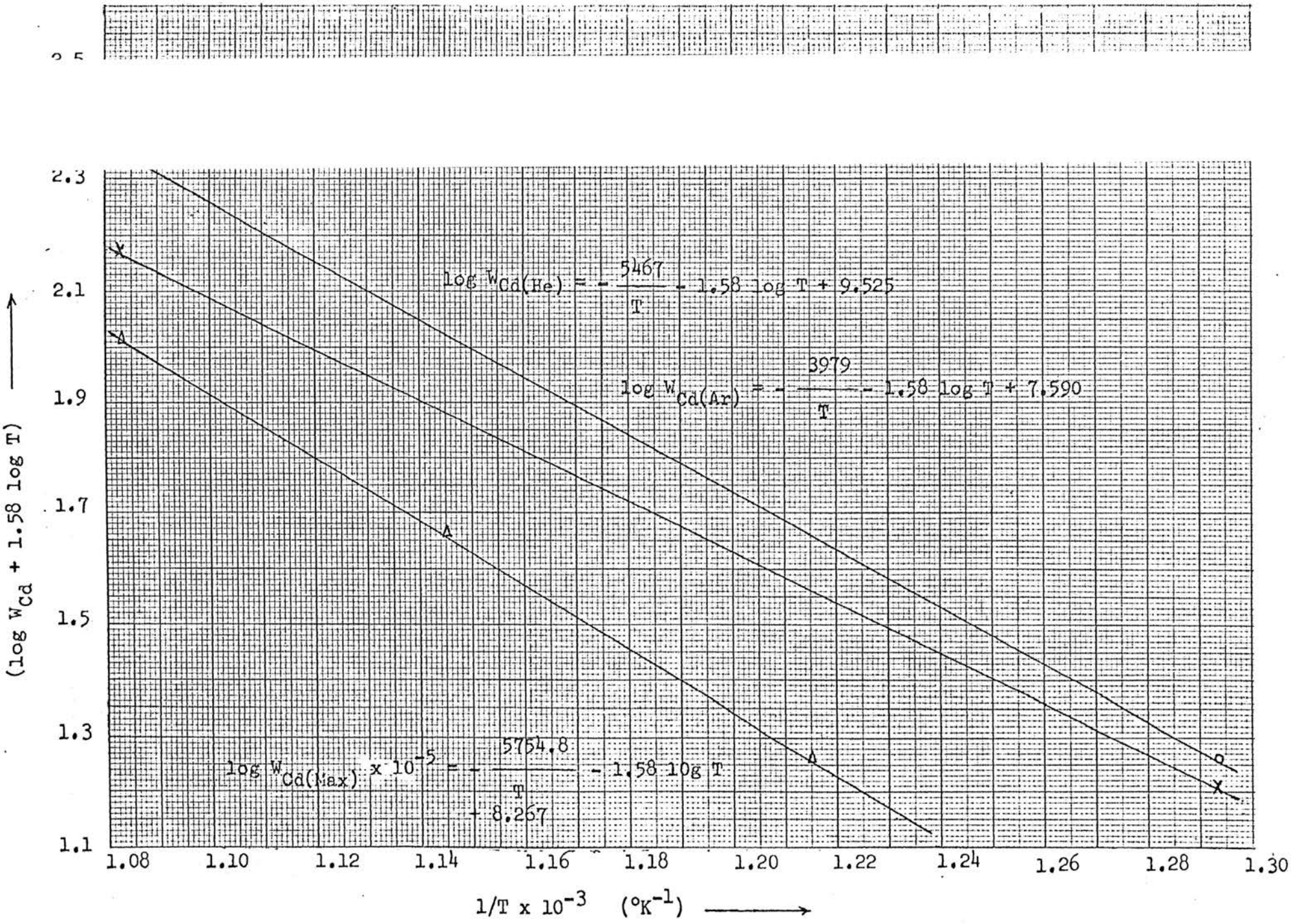


Figure 14 (log W_{Cd} + 1.58 log T) in Argon, Helium, and Vacuum vs 1/T

t be applied to find the lines of best fit for the cases involving and helium. However, the equation of cadmium in argon was found

$$\log W_{Cd_{Ar}} = -\frac{3979}{T} - 1.58 \log T + 7.5907 \qquad (29)$$

arly, the equation for cadmium in helium was found to be

$$\log W_{Cd_{He}} = -\frac{5467}{T} - 1.58 \log T + 9.525 \qquad (30)$$

The changing of the slope of the observed rates was probably due to xidation effect as discussed above.

In Figure 15 Su's[1] observed rates of evaporation of zinc in argon ompared with the author's observed rates of evaporation of zinc in . In Su's investigation the evaporating surface and the condensing ce were not parallel and the effective distance between them was ed to be 7.5 cm. The experimental set-up used in these investigations ifferent. These differences apparently account for the difference en the two curves. If the correct effective distance for Su's experi- is assumed to be 10 cm Su's data will coincide with that obtained in work.

In this investigation a graphite curcible was used so that the tempera- uniformity of the graphite and the metals used should not allow any iable temperature difference to exist within the bulk of the liquid. er, it is possible that the evaporation of the metal could have a ig effect at the evaporating surface. This temperature gradient can imated by the formula[26];

$$\frac{dt}{dx} = \frac{\Delta H_v W}{60 k_c} \qquad (31)$$

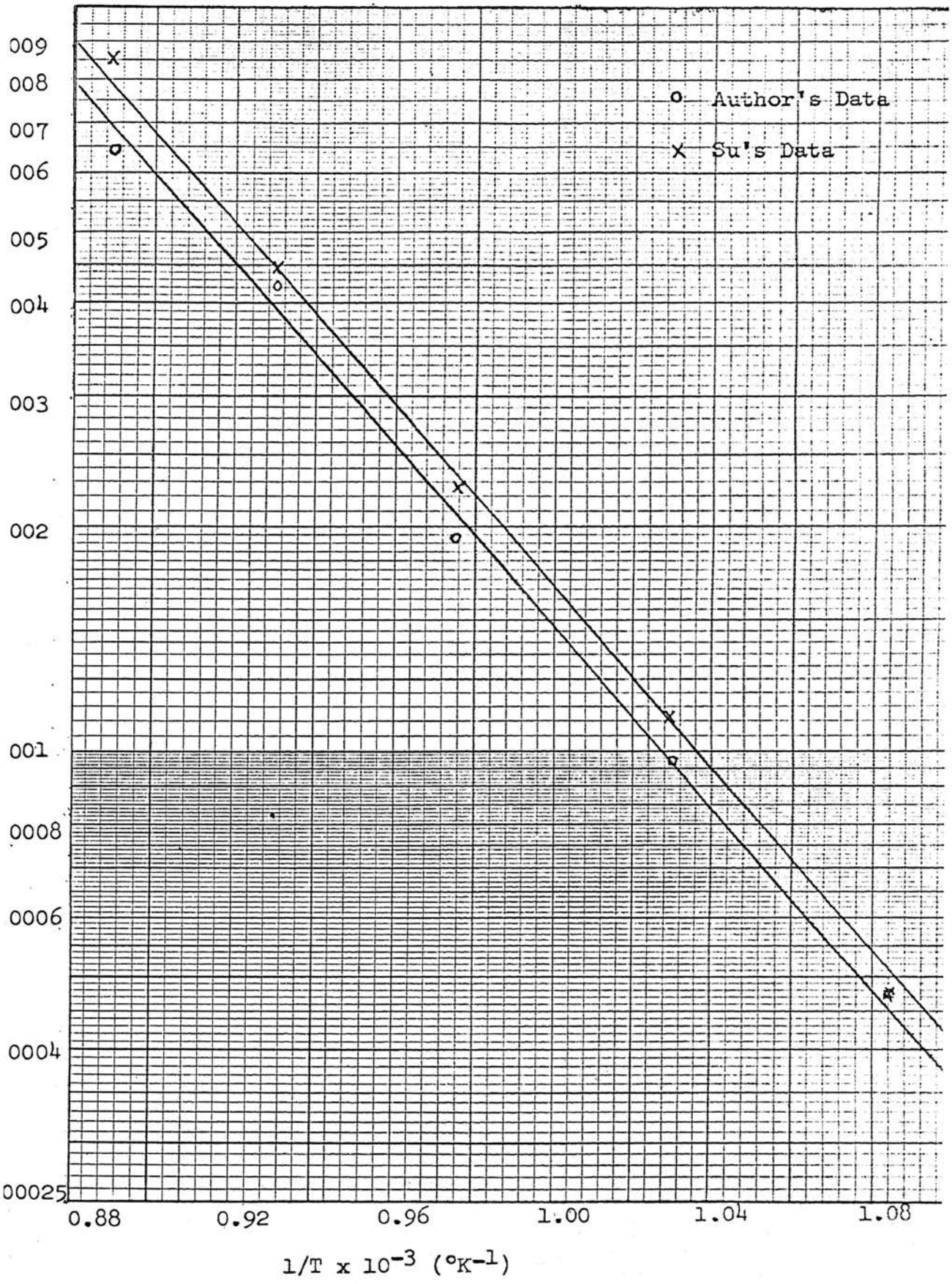


Figure 15 Comparison of the Rate of Evaporation of Zinc in Argon with Previous Data

$_v$ is the heat of vaporization cal/gm,

is the rate of evaporation, gm/cm^2-min, and

is the thermal conductivity, cal/cm^2-sec.

om Equation (31) it is found that the higher the rate of evaporation larger the temperature gradient will be. Since the rates of evan of zinc and cadmium are higher in helium than in argon, it is d that the temperature gradient below the evaporating surface in atmosphere is higher than that in argon.

evaporation of zinc at 650 °C

is approximately 440 calories,

is 0.138 cal/cm^2-sec,

is 4.8×10^{-4} gm/cm^2-min in argon,

is 5.1×10^{-4} gm/cm^2-min in helium,

n

$$\cdot = \frac{440 \times 4.8 \times 10^{-4}}{60 \times 0.138}$$

$= 0.254$ °C/cm

um

$$\cdot = \frac{440 \times 4.8 \times 10^{-4}}{60 \times 0.138}$$

$= 0.271$ °C/cm

nce the difference of the temperature gradient between argon and atmospheres is very small, it is not likely that this difference ffect the evaporating rate to an appreciable extent.

VI. CONCLUSIONS

e rate of evaporation of zinc and cadmium is higher in a helium mosphere than in an argon atmosphere.

e evaporation process in this investigation is thought to be ffusion-controlled.

e rate of evaporation is dependent upon the heat conductivity and e accommodation coefficient of the inert gas.

e experimental results agreed with the calculated values better argon atmosphere than those in helium.

VII. RECOMMENDATIONS

· further study of the evaporation of metals, the following sugges-
·e given to eliminate the uncertainties involved in this investiga-

: condensation of metal vapor before reaching the condenser surface
)uld be avoided in order to assure that all the metal atoms will
ıvel the same distance between the evaporating and condensing surfaces
is also important to measure the condenser temperature. A constant
ıdenser temperature should be maintained. Theoretical equations
: all based on the assumption that the vapor pressure immediately
)ve the condensing surface is zero and that there is no reevaporation
the condensate.
:uration of the residual gases by metal vapor is attained only at
:ero flow rate of the residual gas. Therefore, it is advisable to
ep the flow rate as low as possible.
:dation of the sample surface should be held to minimum. An oxide
lm probably reduces the evaporation rate.
ıce the evaporation of metals is highly temperature dependent, the
ıct evaporating surface temperature should be measured.

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APPENDIX 1

STANDARD DEVIATION

SI $$\frac{-\overline{X})}{\cdot 1}\Big]^{1/2} \qquad (1)$$

Re $$) = \frac{SD}{\overline{X}} \qquad (2)$$

wh

the standard deviation,

the observed rate of evaporation at T, and

the average observed rate of evaporation at T.

F aporation of zinc in argon at 650 °C

$\overline{X} = 0.000500 - 0.000482 = 1.8 \times 10^{-5}$

$\overline{X} = 0.000463 - 0.000482 = -1.9 \times 10^{-5}$

$\overline{X} = 0.000480 - 0.000482 = -0.2 \times 10^{-5}$

$\overline{X} = 0.000480 - 0.000482 = -0.2 \times 10^{-5}$

$\overline{X} = 0.000480 - 0.000482 = -0.2 \times 10^{-5}$

$\overline{X} = 0.000502 - 0.000482 = 2.0 \times 10^{-5}$

$\overline{X} = 0.000473 - 0.000482 = -0.9 \times 10^{-5}$

$\overline{X} = 0.000480 - 0.000482 = -0.2 \times 10^{-5}$

S

$$\left[\frac{(13.94 \times 10^{-10})}{7}\right]^{1/2}$$

1.31×10^{-5}

$$\text{ive SD} = \frac{1.31 \times 10^{-5}}{4.82 \times 10^{-4}}$$

$= 2.72\%$

APPENDIX 2

:ULATION OF THE RATE OF EVAPORATION

te of evaporstion of zinc into an atmosphere containing argon
as dual gas with the total pressure equal to one atmosphere and
th zinc at 850 °C is calculated below.

Th equation is given as

$$\frac{.736\ W_{Zn(Max)}T(1/b)^{2/3}}{\lambda P}\ \frac{(1 + M_{Zn}/M_{Ar})^{1/2}}{[1 * (\rho_{Zn}/\rho_{Ar})^{1/3}]^2} \qquad (3)$$

wh

x) is obtained from equation (2) on page 5:

$$x) = 28.30\ P_{Zn}/T^{1/2}$$

Th ressure of zinc at 850 °C is calculated from equation (4) on
pa

$$n = \frac{-6754.5}{T} - 1.318 \log T - (0.0601)(10^{-3})T + 12.723$$

ar 417.3 mm Hg.

Tr (28.30)(417.3)/(1123)$^{1/2}$

352.4 gms/cm^2-min

Ir 1 (3)

ax) = 352.4 gms/cm^2-min,

123 degree Kelvin,

) cms, the distance from the end of the condenser to the metal surface,

atm = (76)(13.60)(980) dynes/cm^2,

2.19 cm^3/mole,

65.38 gms,

39.94 gms,

$\rho_{Zn} = P_{Zn} M_{Zn}/RT = (417.3)(65.38)/(R)(1123)$,

$\rho_{Ar} = (760 - P_{Zn})M_{Ar}/RT = (342.7)(39.94)/(R)(1123)$.

serting these values into equation (3) gives

$W_1 = 0.00528$ gm/cm^2-min

chak-Langstroth equation is given as

$$W_2 = (9.60)(10^{-4})(P_{Zn})(M_{Zn}D/T\lambda) \qquad (4)$$

xwell's equation is used to calculate the diffusivity. This is given as:

$$D = \frac{kT^{3/2}}{P(V_{Zn}^{1/3} + V_{Ar}^{1/3})^2}(1/M_{Zn} + 1/M_{Ar})^{1/2} \qquad (5)$$

e following values were used in equation (5) to calculate the diffusivity:

k = 0.0047 This is the largest possible value of k[13] and was selecte
to obtain the best agreement with the experimental results.

T = 1123 degree Kelvin,

P = 1 atm,

$V_{Zn} = 65.38/6.7 = 9.75$ cm^3/mole,

$V_{Ar} = 39.94/1.4 = 28.44$ cm^3/mole,

$M_{Zn} = 65.38$ gms,

$M_{Ar} = 39.94$ gms.

ation (5) then gives

$D = 1.257$ cm^2/sec.

values of the other variables in equation (4) have been given above
were used with this value of D to give

$W_2 = 0.00293$ gm/cm^2-min

well-Stefan equaiton is given as:

$$= \frac{(60)(P)(M_{Zn})(D)(P_{Zn850\ °C} - P_{Zn20\ °C})}{(\lambda)(R)(T)(P_{Ar20°C} - P_{Ar850\ °C})} \ln \frac{P_{Ar20\ °C}}{P_{Ar850\ °C}} \qquad (6)$$

e appropriate values of the variables in this equation are

$P = 1$ atm,

$M_{Zn} = 65.38$ gms,

$D = 1.257$ cm^2/sec,

$P_{Zn850\ ^\circ C} = 417.3/760 = 0.548$ atm,

$P_{Zn20\ ^\circ C} \approx 0$ atm,

$P_{Ar20\ ^\circ C} = 1$ atm,

$P_{Ar850^\circ C} = 1 - P_{Zn850^\circ C} = 0.452$ atm,

$\lambda = 10$ cms,

$R = 82.0$ cm^3-atm/degree-gm mole,

$T = 1123$ degree Kelvin.

se values give

$W_3 = 0.00354$ gm/cm^2-min

APPENDIX 3

CALCULATION OF RELATIVE FORCES EXERTED BY RESIDUAL GASES

Since the kinetic energies of gases are the same at a given tempera-
:e, the root mean square velocity of a gas is a function of its tempera-
:e and atomic or molecular weight only.

Equation (7) was used to calculated the root mean square velocity.

$$U = \sqrt{3RT/M} \qquad (7)$$

:re

R is the gas constant 8.3×10^{-7} ergs/gm-mole-deg,

T is the absolute temperature, in degree Kelvin,

M is the molecular weight of gas or vapor, gms.

The root man square velocities of zinc vapor, helium, and argon atoms 850 °C are given as follows:

Gas	Temperature °C	Molecular Weight Grams	U cm/sec
Zn	850	65.38	6.54×10^4
He	850	4.002	2.65×10^5
Ar	850	39.94	8.37×10^4

These molecular weights and root mean square velocities were used equations (8) and (9) to obtain the final velocity of the zinc atoms :er head-on collisions with the residual gas. The initial velocity of :c atom was always taken to be positive and that of the residual gas to negative.

$$M_{Zn}\, U_{Zn} + M_G\, U_G = M_{Zn}\, U_{Zn}' + M_G\, U_G' \qquad (8)$$

$$(1/2)M_{Zn}\, U_{Zn}^2 + (1/2)M_G\, U_G = (1/2)M_{Zn}\, U_{Zn}'^2 + (1/2)M_G\, U_G'^2 \qquad (9)$$

re

U_{Zn} and U_G are velocities of zinc and gas atoms before collision,

U_{Zn}' and U_G' are velocities of zinc and gas atoms after collision.

The velocity of zinc atoms after head-on collision with residual

ses at 850 °C are given below.

Residual Gas	Temperature °C	U_{Zn}'
He	850	15.65×10^4 cm/sec
Ar	850	4.75×10^4 cm/sec

The change in momentum of zinc vapor after one head-on collision was

culated by the relation $M_{Zn}(U_{Zn} - U_{Zn}')$ and the results are given as

lows:

Residual Gas	Temperature °C	Change in Momentum gm/cm/sec
He	850	5.95×10^6
Ar	850	7.38×10^6

Equation (10) was used to calculate the number of collisions per unit

ume per second.

$$Q_{Zn-G} = 1/4(N_{Zn} \times N_G)(\sigma_{Zn} - \sigma_G)\left[\frac{8\pi RT(M_{Zn} - M_G)}{M_{Zn}\, M_G}\right] \qquad (10)$$

re

N_{Zn} is the number of zinc atoms per cm^3,

N_G is the number of gas atoms per cm^3,

σ_{Zn} is the atomic diameter of zinc atom,

σ_G is the atomic diameter of gas atom.

The number of atoms or molecules per cubic centimeter was determined

m

$$N_i = \frac{6.023 \times 10^{23}}{22{,}400}\left(\frac{P_i}{760}\right)\left(\frac{273}{T}\right) \qquad (11)$$

re

N_i is the number of atoms per cm^3,

P_i is the pressure of the residual gas or zinc vapor,

T is the absolute temperature, degree Kelvin,

22,400 cm^3 is the molal volume of zinc vapor or residual gases at the standard conditions.

The number of collision calcualted by using equation (10) at 850 °C given below:

Temperature °C	N_{Zn} cm^{-3}	σ_{Zn} cm	Residual Gas	σ_G cm
850	3.59×10^{18}	2.9×10^{-8}	He	2.18×10^{-8}
850	3.59×10^{18}	2.9×10^{-8}	Ar	3.36×10^{-8}

N_G cm^3	Q_{Zn-G}
2.93×10^{18}	1.86×10^{27}
2.53×10^{18}	3.18×10^{27}

The product of the number of collisions per unit volume per second the change in momentum of zinc atom in a head-on collision with the idual gases was calculated by using equation (12)

$$F_{Zn-G} = M_{Zn}(U_{Zn} - U_{Zn}')(Q_{Zn-G}) \qquad (12)$$

resulsts are given as follows:

Residual Gas	Temperature °C	F_{Zn-G} dynes/cm^3
He	850	1.11×10^{34}
Ar	850	2.35×10^{34}

APPENDIX 4

LIST OF SYMBOLS

Lish Letter Symbols

	Van der Waals' constant
;)	heat capacity of liquid at constant pressure
/)	heat capacity of vapor at constant pressure
	diffusivity in gas
	heat of evaporation
	integration constant
›)$_{Ar}$	integration constant in argon
›)$_{He}$	integration constant in helium
›)$_{vac}$	integration constant in vacuum
	heat of vaporization
ѵ)$_{Ar}$	heat of vaporization in argon
ѵ)$_{He}$	heat of vaporization in helium
ѵ)$_{vac}$	heat of vaporization in vacuum
	thermal conductivity
	constant 0.0036 - 0.0047
	molecular weight
	molecular weight of the metal A
	molecular weight of the gas B
	total pressure
	vapor pressure
	vapor pressrue of zinc
	vapor pressure of cadmium
	partial pressure of zinc
	partial pressure of cadmium

P_T	partial pressure of argon at T degree Kelvin
P_A	partial pressure of the metal A at evaporating surface
P_A'	partial pressure of the metal A at condensing surface
P_B	partial pressure of argon
P_{BM}	log mean partial pressure of the gas B
Q	activation energy of evaporation
R	universal gas constant
T	absolute temperature
V_A	molal volume of the metal A
V_B	molal volume of the gas B
V_V	molal volume of zinc vapor
V_L	molal volume of liquid zinc
W	rate of evaporation
W_{max}	maximum rate of evaporation
W_c	rate of condensation
W_n	net rate of evaporation
W_{Zn}	rate of evaporation of zinc
$W_{(Max)}$	maximum rate of evaporation of zinc
$W_{(Ar)}$	rate of evaporation of zinc in argon
$W_{(He)}$	rate of evaporation of zinc in helium
W_{Cd}	rate of evaporation of cadmium
$W_{(Max)}$	maximum rate of evaporation of cadmium
$W_{(Ar)}$	rate of evaporation of cadmium in argon
$W_{(He)}$	rate of evaporation of cadmium in helium
W_E	Epstein rate of evaporation
W_L	Luchak rate of evaporation
W_M	Maxwell rate of evaporation
X	distance between evaporating and condensing surfaces

density of the metal A

density of residual gas B

VITA

The author was born in Anhwei, Republic of China, on June 14, 1940. hgih school education was completed in 1959 at Provincial Cheng Kung School. In September 1960, he entered Cheng Kung University, located ainan, Taiwan. After graduation with a B. S. degree in Metallurgical neering in June, 1964, he served in the Chinese Air Force for one year. He has been enrolled in the Graduate School of the University of ouri at Rolla since September, 1965.